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International Journal of Plant Nutrition, Plant Chemistry, Soil Microbiology and Soil-borne Plant Diseases

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MULL AND MOR (MÜLLER-HESSELMAN) IN RELATION TO THE SOIL WATER REGIME OF A FOREST

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INTRODUCTION

This paper is an account of investigations into pedological aspects of a wooded area which is being used by a group of workers, of the Institute for Biological Field Research, Arnhem, for the study of the role of the soil microflora and fauna in the breakdown of plant debris, the formation of humus, and the mineralization of soil organic matter.

There are marked differences, over short distances, in the quantity of litter disappearing annually from the soil surface. In some places there seems to be hardly any change in the amount of litter present immediately after leaf fall and the amount remaining the following summer whereas in other places all the litter has disappeared by the following summer; these differences are reflected in the appearance of the A-horizons of the soils. These differences in the litter layers and in the morphology of the A-horizons have been termed "forest-floor types" and they have been described and classified along the lines used by Müller [13] for mull and mor. To differentiate the various forest-floor types encountered it became necessary to subdivide the mull and mor types used by Müller. The distribution of these subtypes has been mapped. Other characteristics of the various subtype sites including topographical relations, texture of the mineral soil, vegetation, reaction (pH), and chemical properties of the soil were recorded. The occurrence of the forest-floor types in relation to the various site characteristics was examined in an attempt to ascertain whether

the development of a forest-floor type is related to the biological or physico-chemical characteristics of a particular site.

This examination showed that a correlation exists between the distribution of the forest-floor types and differences in the water relations of the soils of the oak forest under consideration. Previous investigations (*cf* the review by Handley [2]) do not seem to have considered the possibility of this factor being an agency in determining the differential development of mull and mor.

LOCATION, HISTORY AND GEOLOGY OF THE AREA

At the Institute for Biological Field Research work on the breakdown of plant debris was started in 1942 in other areas but these were abandoned when it was found that they appeared to have been significantly changed by human activity in the more or less recent past.

In 1956 members of the Wageningen Soil Survey Institute came across an area of oak forest situated in the Hackfort Estate in the municipality of Warnsveld, 6 km southeast of Zutphen and 3 km east of the river IJssel and at about 9 m above sea level.

Examination of soil profiles by members of the Soil Survey Institute indicated that the soils of the area, carrying a tree vegetation of pole-stage oak and birch, had not been disturbed by man.

The area, about five acres in extent, was formerly part of the Hackfort Estate, and estate and other records indicate that this particular area of oak wood carried a closed stand of mature, broad-leaved trees in 1809 and has remained under forest ever since. It seems very probable that the area has carried forest since the Middle Ages at least as it has been part of a hunting ground which dates back to the thirteenth century. There are no indications in the records that the area was ever used as arable land or that the trees were rooted up.

Geologically the area is part of the former beds of the river IJssel where Pleistocene river clay and sand are very irregularly distributed. The sands were most probably deposited in pleniglacial times and clay and silt were added in the Bölling period. Deposition of sand may have taken place in the Old Dryas period, the clay and silt dating from the Allerød period *.

Three acres of the area were selected for long-term investigations.

THE TWO MAIN "FOREST-FLOOR TYPES"

In 1887 (p. 82) Müller differentiated the two contrasting humus forms which are to be found in forest soils in the following terms:

"Echter Mull: Nicht über 10% organischer Substanz, ohne freie, auflösliche Humussäure, gut vermischt mit der mineralischen Erde, sowohl durch

* Unpublished account by K. S. Hoeksema.

die Thätigkeit der Tiere wie des Wassers, vollkommen zertheilt, locker, ohne zusammenhang, hauptsächlich Produkt des thierischen Lebens im Boden.

Echter Torf: 30–60% organischer Substanz, enthält freie, auflösliche Humussäure, höchst unvollständig und fast nur durch die Thätigkeit des Wassers mit der Mineralischen Erde vermischt, unvollkommen zertheilt, fest, zähe, zusammenhängend, hauptsächlich vegetablische Schicht''.

Müller apparently based the differential organic matter contents of mull and mor on only a few quantitative data. It would therefore seem that this should be used with caution as a differentiating feature. Further, although organic matter contents of 30 to 60 per cent are given as being characteristic for mor, a value of 13.24 per cent was mentioned in his analysis data (Ref. [13], p. 118). The results of chemical analyses published by Müller indicate that he included the horizon which is nowadays termed A_1 as part of the mor layer.

The mull of Müller can be described as a forest floor in which the uppermost layer of mineral soil, now termed the A_1-horizon, lies beneath no more than a thin, loose layer of litter and has the appearance of mould or loose garden soil; it is friable and inhabited by animals, among which lumbricidae, whose presence is shown by holes and burrows, are always to be found. Mor on the other hand is a coherent upper soil layer, rich in humus and thoroughly interwoven by dark fungal hyphae – a condition which, as Müller pointed out, is outside the sphere of agricultural practice.

Hesselman [5 6] amended Müller's characterization of mull and mor and the following definitions were adopted at the Third International Soil Science Congress in 1935 and are currently used by most soil scientists in the U.K., U.S.A., Scandinavia, and France:

Mull – mixture of organic matter and mineral soil of crumbly or compact structure with the transition to lower layers not sharp.

Mor – organic matter practically unmixed with mineral soil, usually more or less matted or compacted. Transition to mineral soil always distinct. Often composed of two layers named F + H (after Hesselman).

In Germany and Austria however, the classifications of Ramann [14 15] and Kubiena [8 9] are followed. Although Müller's terms are used in some cases in these classifications they have acquired a different meaning. For example, whereas Müller and Hesselman characterized the humus layers of forest and heath soils (A_0- + A_1-horizons) by the macromorphological properties of the two horizons as a whole, the characterization of the soils to which the nomenclature is applied by Ramann and Kubiena is based on the micromorphology of the humus particles and is applied to arable land as well as to forest soils *. Whilst the Müller-

* For detailed descriptions and illustrations see Jongerius [7].

Hesselman conception of mull and mor may also be used for the soils associated with an old grass vegetation or other long established vegetation it is unsuitable for use in connection with tilled land.

Although the morphology of humus particles, as used in the Ramann-Kubiena classification, may be used for the characterization of arable soils it cannot indicate the appearance and nature of the soil or humus layer ($A_0 + A_1$) as a whole as is the case when the Müller-Hesselman classification is used.

Therefore, in order to avoid the confusion which is liable to arise through the use of the term "humus form" this term has been consistently replaced in this paper by the term "forest-floor type".

CHARACTERIZATION OF THE FOREST-FLOOR TYPES OF THE HACKFORT AREA

On the basis of the definitions accepted at the 1935 Congress the forest floor of the Hackfort area, and indeed of the Netherlands as a whole, would probably be separated into the following two types of forest 1) coarse mull and 2) fibrous mor with a thin H-layer ($< 1''$). This degree of separation is inadequate for a detailed classification of the various forest-floor types which are to be found in the area studied. Similar objections apply to the classifications of Romell and Heiberg [16], Heiberg [3], Heiberg and Chandler [4], Lutz and Chandler [10], Ehwald [1], and Wilde [19].

The different forest-floor types to be found at Hackfort have therefore been described and provisional names given to them as follows:

Forest-floor type Mull

Subtype 1) Common Mull. F- + H-layers absent; A_1-horizon crumbly with the greatest concentration of finely divided organic matter, thoroughly mixed with the mineral soil, in the upper part of the horizon. Litter falling in autumn has disappeared from the soil surface before the next leaf fall. Common mull is itself subdivided into acid mull and mull rich in lime depending on the occurrence of $CaCO_3$ or a high content of Ca^{++} in the A_1-layer.

Subtype 2) Mull rich in litter. L-layer and a very thin F-

layer present. Coarse particles of organic matter are mixed with the mineral soil in the crumbly top of the A_1-horizon. When the leaves fall in the autumn litter from the previous leaf fall still remains on the soil surface. This subtype is intermediate between common mull and light mor. Beneath the litter layer the soil is crumbly and loose and mouse holes are often present. The A_1-horizon is always some shade of brown in colour.

Forest-floor type Mor

Subtype 3) Light mor. L-, F- and H-layers are present and clearly distinguishable from the A_1-horizon. The F_x- and H-layers are matted but not so markedly as in common mor nor are they coloured such dark shades of brown. The structure of these layers is more or less loosely and they contain many fine roots and dark-coloured fungal hyphae. Under damp conditions it is possible to smear the greasy material lying at the boundary between the H-layer and the A_1-horizon over the surface of the mineral soil with a finger. The A_1-horizon tends to be coloured dark brown to black.

Subtype 4) Common mor. F_x- and H-layers strongly developed and compacted, containing fine roots and interwoven by numerous, dark-coloured fungal hyphae. The boundary with the A_1-horizon is very greasy and readily smears when damp. The A_1-horizon is black in colour due to inwashed organic matter.

Subtype 5) Mor poor in humus. Generally only a small amount of litter is present and well-developed F- and H-layers as well as a greasy boundary region with the A_1-horizon are lacking. The black colour of the A_1-horizon is due to humus material probably carried downwards solely by percolating water. The A_1-horizon often has a loose structure, due to the coarse sand from which it has developed, but never has the characteristics of mull and is interwoven by numerous, dark-coloured fungal hyphae similar to those present in subtypes 3 and 4. The total carbon content, down to the depth at which organic matter ceases to occur, is about 3.6 kg per square meter. In the Hackfort area this subtype is almost entirely restricted to the very coarse, low-lying sands.

METHODS

Methods used for the chemical analysis of the soils

Sampling. The position of each quadrat was indicated in the field by a wooden marker. Three samples, each of about 25 ml in volume and from the 0–5 cm depth of the A_1-horizon, were taken just around each quadrat marker. The three samples were bulked for analysis giving a total of 126 samples. For the determination of the amount of carbon occurring in the soils to a depth of 40 cm, 8 cores covering the 0–40 cm depth (including the A_0-, L-, F- + H-layers) were taken from 16 sampling areas and bulked. In August samples of the A_0 and samples of the coarse plant remains (> 2 mm) from the upper 5 cm of the soil were taken from the various quadrats for carbon determinations. One complete series of samples for the determination of reaction (pH) was taken in April and another series in June 1957.

Reaction (pH). The reactions of the soil samples were determined in the presence of 1 *N* KCl (glass electrode).

Cations and anions. Values for the amounts of the more important cations and anions present in the soil samples were obtained by treating the samples by the acetate buffer method of Morgan [12] and Venema [18].

Carbon. The carbon contents of the various soil samples were determined by the dry-combustion method and by the wet-oxidation method of Mebius *et al.* [11].

Nitrogen. The total-nitrogen content of the soil samples was determined by the Kjeldahl method.

Methods used in the assessment of other soil characteristics

Texture. The texture of the soils was assessed in the field by kneading and rolling a small amount of soil between the thumb and fingers. Only three texture classes were distinguished:

1. loamy sand; 2. fine sand; 3. coarse sand.

Colour of the upper part of the A_1-horizon. The colour of the soil samples was assessed, in both wet and dry conditions, by means of the Munsell colour charts.

Degree of leaching. Three degrees of leaching, which are characterized as follows, were assessed by visual examination:— *Weak* – no visible leaching of the mineral particles which are all covered by a brownish film. *Moderate* – some of the sand grains are not covered by a brownish film and have a whitish, bleached appearance. *Strong* – almost all the sand grains are bleached and white in colour.

Topography. The lowest point in the area was taken as the zero level and the height of all other soil surfaces above the zero level was measured in cm.

Depth of the water table. The depth of the water table below the soil surface was measured in cm at various times of the year.

Characterization of the vegetation of the area and observations on leaf fall and root development

Timber volume. The standing volume, in cub. dm per 100 m square quadrat, of the various tree species was measured by Dr. Luitjes. The relative volumes for each species present on the quadrats were calculated as percentages of the maximum volume of timber encountered on any of the quadrats.

Leaf fall. In 14 places in the area the leaves *etc.* shed by the trees are caught in cheesecloth sacks with a circular opening of 0.5 sq.m. The sacks are in continual operation for 3.5 years in succession. Weekly or monthly the amount of leaves fallen into the sacks is weighed and sorted to tree species.

The depth to which roots developed was ascertained for various quadrats.

RESULTS

The distribution of the various forest-floor subtypes over the area is shown in Fig. 2.

Soil analyses

It is not practicable to present the data for all the chemical analyses and only the analytical results for typical quadrats are given in Table 1, column I, the quadrats being indicated by the grid numbers used on the map of the area (see Fig. 1).

Reaction (pH). The results for the pH measurements are given in Table 1, column III and in Table 2. Only the mull rich in lime gives pH values which are appreciably different – less acid – from those for the other sites. The acid mull cannot be distinguished from the other forest-floor subtypes on the basis of the pH (KCl) values. This becomes clear when average values for the various forest-floor types occurring in the 126 quadrats are considered. The differences between the pH values obtained for the acid mull and those for the common mor are very small even though the differences in ground flora are very pronounced. Even in the case of the acid mull and the mull rich in litter, where the pH values differ by only 0.1 pH unit, the luxuriance and species composition of the herbaceous ground flora is considerably richer on the acid mull. On the other hand the similarity of the herbaceous ground vegetations of the mull rich in lime and the acid mull does not lead one to suspect the difference of nearly 4 pH units between their reactions.

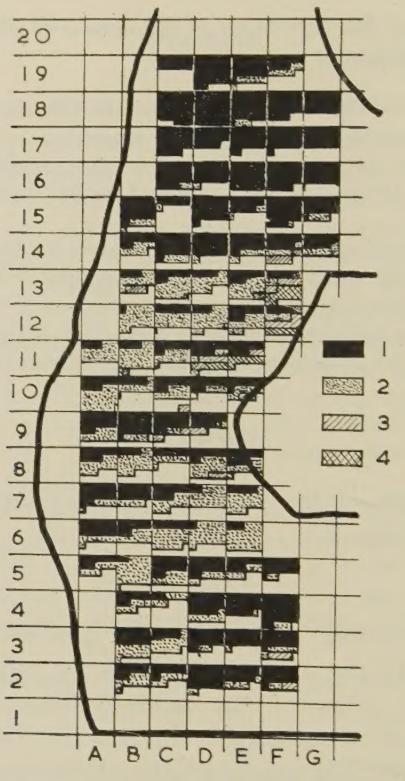

Fig. 1. The volume of wood of oak, birch, poplar, and alder found on the various quadrats. The volume for each species on each quadrat is expressed as a percentage of the maximum volume which occurs on any quadrat *i.e.* 3000 cub. dm on quadrat D18 = 100%. Thus quadrat F12 has only 80% of the maximum observed volume on D18 and 16% is oak, 18% is birch, 26% is poplar and 20% is alder.
1 = oak, 2 = birch, 3 = poplar, 4 = alder.

Kations and anions. In column IV (Table 1), some data are given concerning the local content of lime. In column V is seen that the quantities of calcium ions dissolved in the Morgan-Venema buffer solution differ strongly, but it is still difficult to find an essential difference between the acid types. The magnesium ions in column VI show a tendency to higher values in the mor types. To a lesser degree the same holds for the phosphorus in column VII. Potassium in VIII and iron in column IX are irregularly distributed. Manganese content in column X decreases with increasing height.

TABLE 1

Chemical and other soil characteristics of the various forest-floor subtypes

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII		XIX
Square code no.	Forest-floor type	pH (KCl)	$CaCO_3$ %	CaO ppm	MgO ppm	P_2O_5 ppm	K_2O ppm	Fe_2O_3 ppm	Mn_2O_3 ppm	Carbon %, 0–5 cm (dry comb.)	Carbon %, 0–40 cm (dry comb.)	Carbon in litter g/m² (dry comb.)	Carbon total kg/m² (dry comb.)	Carbon, relative degree of oxidation of	C:N ratio in soil 0–5 cm	Height above zero level in cm	Water table depth in cm from soil surface		Texture 1 = loamy 2 = fine 3 = coarse sand
																	Min.	Max.	
D10	Mull rich in lime	6.8	10.6 / 2.6	> 500	10	2.5	18	1.5	10	3.5	1.09	900	5.75	83	20.1	20	24	125	1 2
E12	id.	5.2	—	500	10	2.5	25	8	10	3.1	.68	970	4.02	77	15.7	12	28	129	2/3
D2	Common mull (acid)	3.4	—	150	16	1.8	18	13	8	2.5	1.17	875	6.20	81	15.6	20	—	—	1
F2	id.	3.3	—	300	16	2.5	22	15	6.5	2.9	1.42	640	7.21	74	18.2	15	—	—	1,2
A12	id.	3.7	—	400	16	3.7	18	8	8	3.0	1.44	440	5.51	75	13.8	20	—	—	1/2
B12	id.	3.6	—	300	14	2.5	20	10	—	—	1.35	680	5.30	82.5	—	15	—	—	1
D4	Mull rich in litter	3.4	—	300	35	5	40	27	8	3.8	1.14	830	6.00	68	—	15	32	137	1
B5	id.	3.8	—	325	16	1.2	35	21	3	4.1	1.21	920	5.77	89	—	30	—	—	2
C12	id.	3.4	—	500	20	2.5	35	4	9	3.4	.83	710	4.29	125	—	15	—	—	2
A8	Light mor	3.2	—	210	35	3.4	46	13	5	9.7	1.21	1680	6.51	93	—	35	—	—	2
B7	id.	3.4	—	500	35	1.5	46	13	2	8.5	1.20	2060	7.11	90	—	30	—	—	2
B14	id.	3.2	—	130	28	4	18	8	2	11.6	2.77	2060	12.26	102	30.4	50	68	> 163	2
C17	id.	3.2	—	100	55	5	18	13	1.5	11.0	2.29	1690	9.20	84.5	23.1	35	—	—	2/3
D18	Common mor	3.3	—	95	35	5.5	< 18	5	1.5	—	1.10	1710	6.50	77	—	55	71	> 163	2
D19	id.	3.4	—	250	70	5	42	8	1.5	14.8	3.89	2070	12.54	90	21.2	50	—	—	2
G16	Mor poor in humus	3.2	—	300	45	5	42	10	3	—	.56	900	3.67	87.5	—	20	—	—	3

TABLE 2

Mean pH(KCl) values for the various forest-floor subtypes occurring in the 126 quadrats							
Forest-floor types	1 Mull rich in $CaCO_3$	2 Mull at border region of 1	3 Acid mull	4 Mull rich in litter	5 Light mor	6 Common mor	7 Mor poor in humus
April 1957 . .	7.2	4.7	3.46	3.4	3.25	3.25	3.2
June 1957 . .	6.6	4.5	3.4	3.3	3.3	3.1	3.15

It is difficult to judge the essential influence of the regularities in manganese and magnesium contents in the causality of the different forest-floor types. At the moment the author is inclined to think their influence to be negligible.

Carbon and organic matter. The carbon content of the uppermost 5 cm of the A_1-horizons in the various quadrats is expressed as a percentage of the oven-dry soil in Table 1, column XI. The carbon content of the 0–40 cm depth of soil is similarly expressed in Table 1, column XII.

The carbon contents of the litter and coarse plant remains (> 2 mm) present in the uppermost 5 cm of the A_1-horizon are given, for the various quadrats, in g of carbon per sq.m in Table 1, column XIII; the total weight of carbon to a depth of 40 cm, which also includes that of the surface organic layers, is similarly expressed for the various quadrats in column XIV. The values obtained for both these quantities show discernible differences between the samples from the mull sites and those from the mor sites although it is not possible to distinguish the various subtypes of these two groups on the basis of these values. The mean value for the total-carbon content for the various acid-mull and mull-rich-in-litter sites is 5.75 kg/sq.m and that for the various light-mor and common-mor sites is 9.02 kg/sq.m. If the carbon contents of the surface organic layers are excluded the values become 5.02 and 7.1 kg/sq.m respectively. In both cases the mor forest-floor types contain more carbon than the mull forest-floor types.

It is not possible to determine the exact amount of organic matter in soil by direct analysis, usually the percentage of carbon found is converted by a conventionally accepted standard factor into percentage of organic matter. As differences in the nature

of the organic matter in the various forest-floor types occurred to exist the concept of the *relative degree of oxidation* of the soil carbon has been introduced. This is defined as the ratio of the percentage of carbon found by wet combustion (Mebius *et al.* [11]) to that found by dry combustion multiplied by 100. Values for this ratio for the various forest-floor types are given in Table 1, column XV. The lower values for this ratio indicate the presence of organic matter relatively rich in oxygen; thus the organic matter of the soil of quadrat D4 with a relative degree of oxidation of 68 should be in a condition twice as oxidized as the organic matter of quadrat C12 with a relative degree of oxidation of 125. On this basis the organic-matter content of the soil computed from the carbon content of the soil and the conversion factor 1.724 is not reliable; such a method can only be used in special circumstances (see also Mebius *et al.* [11]).

C N ratio. The C N ratio was calculated from the total-nitrogen content of the soil and the carbon content as determined by the dry-combustion method. The ratios obtained in this way vary from 13.8 to 30.4 and contrary to expectations, the ratio for the mull rich in lime (quadrat D10) is rather high (20.1) and further investigations are required to ascertain whether such a ratio is usual for soils of this kind.

Topography

The heights of the various quadrats above the zero level and their relationships to each other are shown in Fig. 3.

Depth of water table

The maximum and minimum depths of the water table below the soil surface are given in Table 1, column XVIII. Water tables near to the surface of the soil only occur in winter.

Distribution of roots

The greater part of the root system occurs between a depth of 40 to 50 cm and the soil surface but roots do go down to a depth of 120 cm. On those areas which are at the highest levels above the zero level the deepest roots will go down somewhat lower than 120 cm.

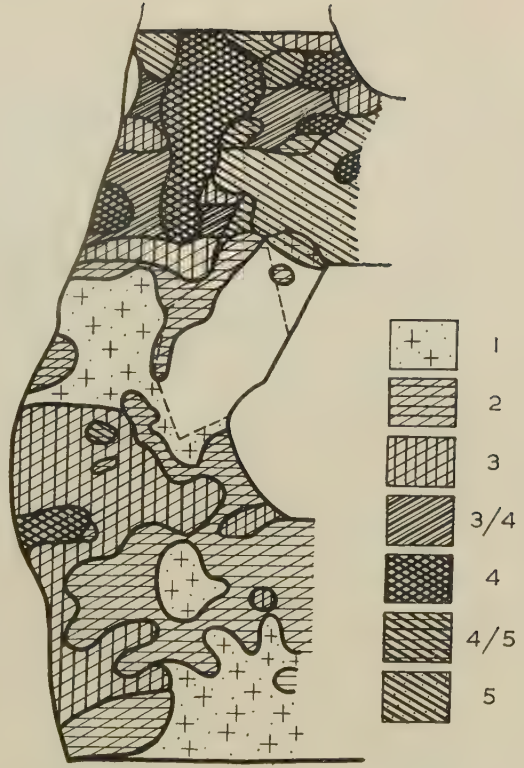

Fig. 2. The distribution of forest-floor subtypes from field records.
1 = common mull, 2 = mull rich in litter, 3 = light mor, 4 = common mor, 5 = mor poor in humus. Transitions are indicated by 1/2, 4/5 *etc.*

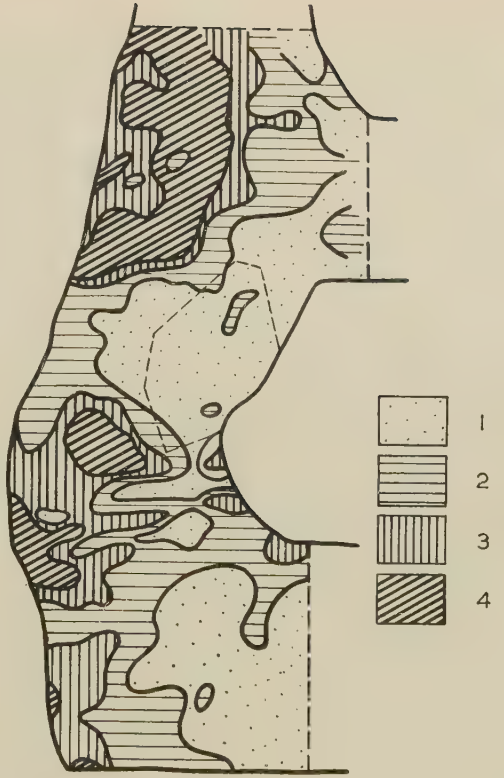

Fig. 3. Topography of the site in four height classes above the lowest level.
1 = 0–20 cm 3 = 30–40 cm
2 = 20–30 cm 4 = 40 cm and more

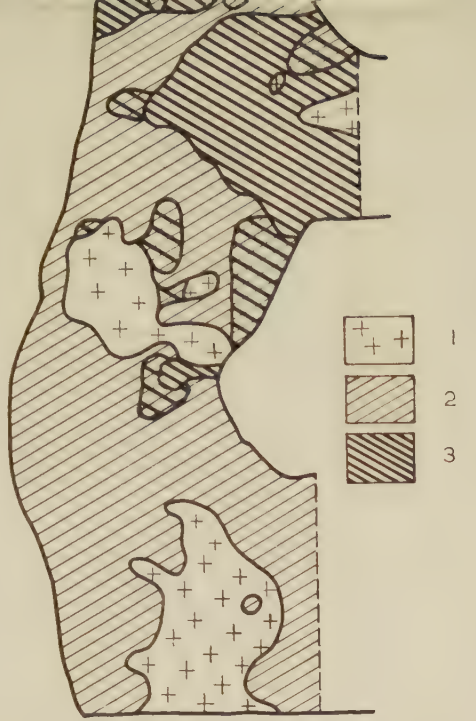

Fig. 4. Map showing the texture of the soils of the area.
1 = loamy sand, 2 = fine sand, 3 = coarse sand.

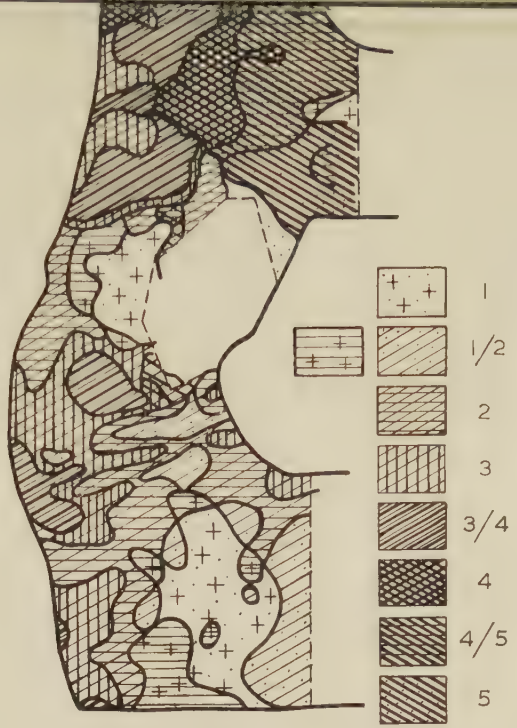

Fig. 5. Distribution of forest floor subtypes predicted from superimposition of maps of soil texture and height of soil surface above the zero level.
1 = common mull, 2 = mull rich in litter, 3 = light mor, 4 = common mor, 5 = mor poor in humus. Transitions are indicated by 1/2 *etc.*

Soil texture

The texture of the mineral material of the soils of the various quadrats is given in Table 1, column XIX and the distribution of the three texture classes is shown in Fig. 4.

Soil colour

The colour of the soil of the various quadrats was recorded as it appeared to assist in the differentiation of the forest-floor subtypes. In the case of soils having the same texture and developed from the same kind of sand, differences in colour will be a reflection of differences in the nature of the humus and of differences in the processes of decomposition of organic matter. The following colours were recorded for the upper 3 cm of the various A_1-horizons:

1. grey (very dark grey 10 YR 3/1 and 10 YR 4/1);
2. dark ochre (yellowish brown 10 YR 4/4 and 10 YR 4/4);
3. light brown (yellowish brown 10 YR 3/4 and 10 YR 4/3);
4. dark brown (very dark greyish brown to dark brown 8.75 YR 3/2 and 10 YR 3/2);
5. black (black 5 YR 2/1.5 and 7.5 YR 3/1).

The field names are mentioned first and between the brackets the first colour recorded is that of the soil when wet, the second being the colour of the same soil when dry, both expressed in the Munsell notation.

Vegetation and leaf fall

The maximum standing volume encountered on a quadrat was 3000 cub. dm on quadrat D18. The standing volumes for each species on the various quadrats are shown in Fig. 1.

A detailed description of the ground vegetation of the various quadrats will be published elsewhere. The total amount of leaves shed annually in the various quadrats is perhaps 10 per cent more on mull than on mor sites. The annual mean over 3 years is 315 g/sq.m (oven-dry weight).

DISCUSSION

Although the data in Table 1 indicate differences between the various forest-floor subtypes they give no obvious clue to the reasons for their differential development.

In the opinion of the author, the species composition of the herb vegetation is controlled by the same factors which are responsible for the differential development of the forest-floor subtypes. Since details of the floristic composition of the ground flora are to be published elsewhere this will not be discussed further here.

The information collected from the various estimations and examinations was transferred to punched cards.

On each card all the information regarding a quadrat, including forest-floor subtype, soil texture, soil colour, degree of leaching of soil, height of soil surface above zero level, reaction of soil (pH), and the tree species occurring, was recorded. For the sake of brevity the characteristics forest-floor type, texture, colour of A_1-horizon, and degree of leaching were represented, in this order of sequence, by numbers which indicated the relative values, which had already been assigned to them from field observations for these characteristics for a particular quadrat. For example a quadrat having a forest-floor subtype 4 (common mor) which had developed on mineral material with texture 3 (coarse sand) and exhibiting colour 5 (black) and a degree of leaching 3 (strong) would be represented by 4-3-5-3.

Generally where the site characteristics of a quadrat had intermediate values, *e.g.* fine sand with clay or light- to dark-brown in colour, the punched cards for such quadrats were not used in compiling the tables of results in order to avoid confusion. Consequently the different tables of results are not always derived from the same set of punched cards. Any trends suggested by the cards for quadrats having transitional characteristics do not conflict with, indeed they support, the conclusions ultimately drawn.

TABLE 3

equency of association of the various categories of texture, colour and degree of leaching of the A_1-layer from the field observations for the various quadrats

ture	1. Loamy sand			2. Fine sand			3. Coarse sand		
ree of aching . . .	Weak (1)	Moder-ate (2)	Strong (3)	Weak (1)	Moder-ate (2)	Strong (3)	Weak (1)	Moder-ate (2)	Strong (3)
our:									
Grey * . .	1	—	—	3	—	—	1	—	—
Dark ochre	—	—	—	1	—			–	
Light brown	*15*	—	—	7	—	—	—	—	—
Dark brown	3	—	—	*20*	8	1			
Brown/black	1	—	—	—	*12*	2	—	—	3
Black . . .	—	—	—	—	—	*8*	—	—	*18*

The grey soil colour is only found in places rich in lime (pH > 7.0).

The field observations when assembled on punched cards were first used to ascertain the frequency of association of the various categories of soil texture, colour of the A_1-horizon and degree of leaching in the various quadrats. These are set out in Table 3 and it will be observed that there is a strong tendency for loamy sand with a light brown A_1-horizon to be associated with weak leaching, for fine sand with a brownish-black A_1-horizon to be associated with moderate leaching, and for coarse sand with a black A_1-horizon to be associated with strong leaching. The table also indicates that whereas loamy sand is only associated with weak leaching, fine sands may exhibit all degrees of leaching and coarse sands are always strongly leached; the only exception being a coarse sand rich in chalk where, as is to be expected, leaching was not visible. The other soils show that an increase of degree of leaching is associated with a darkening of the topsoil. The loam soils are mostly light brown in colour, the fine sandy soils tend to be dark brown or blackish in colour and the coarse sands are predominantly black. Thus the colour of the upper part of the A_1-horizon and its degree of leaching seem to be related to its texture. In view of this relationship the association of these soil characteristics with the various forest-floor subtypes was studied and the results are set out in Table 4. The results indicate that the forest-floor subtypes are more strongly related to soil texture than to soil colour or degree of leaching. The association of certain combi-

TABLE 4

Frequency of association of the various forest-floor subtypes with different combinations of the various categories of three soil characteristics

Texture	Loamy sand		Fine sand					Coarse sand
Colour of upper part of A_1-horizon	Grey	Light brown		Dark brown	Brown/ black	Black		
Degree of leaching	Weak				Moderate		Strong	
Code	-1-1-1	-1-3-1	-2-3-1	-2-4-1	-2-4-2	-2-4/5-2	-2-5-3	-3-5-3
Forest-floor subtype:								
1. Common mull	4	10	7	3	—	—	—	—
2. Mull rich in litter	—	5	1	17	1	1	—	—
3. Light mor	—	—	—	—	8	11	—	1
4. Common mor	—	—	—	—	—	—	8	2
5. Mor poor in humus	—	—	—	—	—	—	—	9

nations of the three soil characteristics with particular forest-floor subtypes becomes apparent.

The association of the two forest-floor subtypes common mull and mull rich in litter with the same combination (1 : 3 : 1) of soil characteristics *i.e.* loamy sand with light-brown toplayer of the A_1-horizon and weak leaching, is somewhat confusing. The five quadrats C5, D4, E5, E6 and F5 are the only ones where mull rich in litter occurs on loamy sand and in these quadrats the loamy sand is rather sandy which makes it rather difficult to judge to which texture class it belongs.

It is evident that common mull and a form more transitional to mull rich in litter are associated with loamy sand and in addition that whilst the colour of the top of the A_1-horizon of these forest-floor subtypes is light brown for the acid quadrats it is grey for the alkaline quadrats.

Fine sand is associated with all the forest-floor subtypes except mor poor in humus. Each of the other forest subtypes on fine sand show a close association with certain combinations of colour and degree of leaching.

Whilst it is not very clear cut, the tendency for texture to be associated with forest-floor subtypes, as it was found to be associated with colour of the A_1-horizon and degree of leaching, can be observed in Table 4 although the frequency of association of the forest-floor subtypes with coarse sand is not easily understood. It was expected that common mor would be most frequently associated with coarse sand but in fact mor poor in humus holds this position. However, the forest-floor subtype mor poor in humus is difficult to classify and in some ways seems to be more closely related to light mor than to common mor.

The frequency of association of the various categories of the three soil characteristics – texture, colour of the upper part of the A_1-horizon and degree of leaching - with quadrats having soil surfaces at various heights above the zero level was also studied. Though the differences in heigth above the zero level are small, 60 cm at the most, they were divided into 12 classes each differing by 5 cm. The results are shown in Table 5 and there seems to be a correlation between the heigth classes and certain combinations of the categories of texture, colour of the upper part of the A_1-horizon, and degree of leaching.

TABLE 5

Frequency of association of various soil-surface height classes with different combinations of the various categories of three soil characteristics

Height classes (differing by 5 cm)	Combinations * of the categories of the characteristics texture, colour of the A_1-horizon, and degree of leaching							
	-1-1-1	-1-2-1	-2-3-1	-2-4-1	-2-4-2	-2-4/5-2	-2-5-3	-3-5-3
12 (= > 60 cm)	–	–	–	–	–	–	–	–
11	–	–	–	–	–	–	2	1
10	–	–	–	–	2	1	2	1
9	–	–	–	–	–	2	3	5
8	–	–	–	–	–	1	–	1
7	–	–	1	5	–	3	1	5
6	–	2	1	5	3	3	–	–
5	–	5	1	2	1	3	–	–
4	2	5	3	5	1	1	–	1
3	1	2	–	3	–	–	–	1
2 (= < 10 cm)	1	–	–	–	–	–	–	–

* E.g. -1-1-1 means: texture 1 (loamy sand); colour 1 (= grey); degree of leaching 1 (= weak).

TABLE 6

The frequencies with which the various categories of the quadrat characteristics are associated with the different height classes of the soil surface above the zero level

Height classes (differing by 5 cm)	Forest-floor subtypes *					Texture **			Colour of the A_1-horizon †					Degree of leaching ‡			Vegetation §		
	1	2	3	4	5	1	2	3	1	2	3	4	4/5	5	1	2	3	1	2	3
12	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
11	–	–	1	3	–	–	3	1	–	–	–	–	–	6	–	1	3	3	–	–
10	–	–	2	3	–	–	5	–	–	–	–	2	2	8	–	1	4	4	1	1
9	–	–	1	3	2	–	4	2	–	–	–	–	3	11	–	1	5	6	–	–
8	–	–	3	1	–	–	3	1	–	–	1	–	1	2	–	–	1	1	–	–
7	1	7	5	1	1	1	12	2	–	–	1	6	6	9	6	3	3	7	–	–
6	2	6	4	–	–	2	8	–	–	–	5	9	5	–	6	4	–	4	4	–
5	6	2	3	–	2	5	6	2	–	–	7	5	6	2	8	4	2	5	5	1
4	11	7	–	–	1	10	7	2	2	–	8	7	–	1	16	2	1	9	4	3
3	8	3	1	–	–	4	7	1	3	–	2	5	–	1	7	1	–	3	2	4
2	2	–	1	–	–	–	2	1	2	–	1	1	–	1	–	1	–	1	–	2

* Forest-floor subtypes: 1 = common mull, 2 = mull rich in litter, 3 = light mor, 4 = common mor, 5 = mor poor in humus.

** Texture: 1 = loamy sand, 2 = fine sand, 3 = coarse sand.

† Color (field names): 1 = grey, 2 = dark ochre, 3 = light brown, 4 = dark brown, 4/5 = dark brown to black, 5 = black.

‡ Degree of leaching: 1 = weak, 2 = moderate, 3 = strong.

§ Vegetation: 1 = oak, 2 = birch, 3 = alder and poplar.

Table 6 shows the frequency with which the various categories of the quadrat characteristics are associated with the various height classes above the zero level in order that the characteristics most strongly associated with height class might be ascertained.

The frequencies for the various characteristics are not all derived from the same quadrats since transitional values between categories of a characteristic are not included.

For an occurrence of oak or birch to be recorded in the "vegetation" column of Table 6 more than 50 per cent of the quadrat had to be covered with oak or birch. For an occurrence of alder and poplar to be recorded these species had to be substantially present among the oak and birch.

On the quadrats which are highest above the zero level oak predominates whereas on the lower quadrats either oak or birch may be dominant.

Although loamy sand does not occur above height class 7 (35 cm above zero level) the fine and coarse sands occur rather uniformly throughout the height classes. Very coarse sand in layers 30 to 60 cm thick, occurring in height classes 2 to 9, is associated with mor poor in humus.

The open line across Table 6 roughly divides the quadrats with weak or moderate leaching from those with strong leaching. When strong leaching occurs below the open line it is predominantly associated with mor poor in humus. Below the open line the upper zones of the A_1-horizons are predominantly in the colour categories 3 and 4 whereas in the height classes above the open line they are predominantly in the colour category black. Grey colours are restricted to the soils on quadrats rich in lime.

The soil characteristics which show the closest parallel distribution of frequency in relation to height of the soil surface above the zero level are the colour of the upper part of the A_1-horizon and the subtype of the forest floor. Each forest-floor subtype is associated with a particular colouring of the upper part of the A_1-horizon and variation in both characteristics seems to be similarly associated with variation in heigth class.

In contrast to the characteristics height of soil surface above zero level and soil texture, the colour of the upper part of the A_1-horizon and the degree of leaching are the products of soil processes which have occurred since the sand and clay were deposited.

It is logical to conclude that the vegetation may have had some influence on the development of the colour and degree of leaching of the soils. The frequency with which various soil colours are associated with a vegetation predominantly oak or birch growing on soils of different textures will be apparent from Table 7. The

TABLE 7

The frequencies with which A_1-horizons of different colours are associated with a vegetation predominantly oak or birch on soils of different textures

Texture	1. Loamy sand		2. Fine sand		3. Coarse sand	
Vegetation	Birch	Oak	Birch	Oak	Birch	Oak
Colour:						
1. Grey	—	1	—	—	—	—
2. Dark ochre	—	—	—	—	—	—
3. Light brown	3	9	1	1	—	—
4. Dark brown	1	2	5	1	—	—
4/5. Dark brown to black	—	—	3	4	—	—
5. Black	—	—	—	6	—	7

soils developing on loamy sand under both tree species are most frequently light brown in colour whilst the soils developing on fine sands are most frequently dark brown under birch and blackish under oak. The blackest soils have developed on coarse sand where only oak is growing.

The modifying influence of tree species on the strong correlation between degree of leaching and soil texture is shown in Table 8.

TABLE 8

The frequencies with which various categories of degree of leaching are associated with oak and birch on soils of different textures

Texture	1. Loamy sand		2. Fine sand		3. Coarse sand	
Vegetation	Birch	Oak	Birch	Oak	Birch	Oak
Degree of leaching:						
1. Weak	4	12	5	2	—	—
2. Moderate	—	—	4	3	—	—
3. Strong	—	—	—	7	—	7

Since forest-floor subtypes, height classes *etc.* are most clearly differentiated on the fine sandy soils the information for quadrats on these soils has been examined in greater detail.

It will be seen from Table 9 that in the case of mull forest floors developed on fine sand the quadrats are at a low level above

TABLE 9

The categories of the soil characteristics forest-floor subtype, colour of the A_1-horizon, and height class associated with the various degrees of leaching and the vegetation types birch and oak in soils developed on fine sand

Texture . . .	Fine sand					
Vegetation . .	Birch			Oak		
Degree of leaching	Forest-floor subtype *	Colour of A_1-horizon	Height class	Forest-floor subtype	Colour of A_1-horizon	Height class
1. Weak . .	1	3	5	1	3	4
	2	4	5	2	4	4
	2 (3 ×)	4	6	—	—	—
2. Moderate .	3	4	10	3	4/5	6
	3 (2 ×)	4/5	5	3	4/5	7
	3	4/5	6	3	4/5	10
3. Strong . .	–	–	–	4 (3 ×)	5	9
	–	–	–	4 (3 ×)	5	10
	–	–	–	4	5	11

* Of the forest-floor subtypes the occurrence of higher frequencies are indicated between brackets.

the zero level and the colour of the upper part of the A_1-horizon is rather light. For soils developing on fine sand and only weakly leached, the forest-floor subtype mull rich in litter is associated with both oak and birch. The colour of the upper part of the A_1-horizon is the same under both tree species. The height of the quadrats above zero level is somewhat lower for those carrying oak than for those carrying birch. Fine sandy soils situated at the same height above the zero level and showing a moderate degree of leaching will, under both tree species, be similarly coloured in the upper part of the A_1-horizon and associated with a light mor.

On strongly leached soils oak is by far the predominant species and the trend just mentioned continues *i.e.* the colour of the upper layer of the A_1-horizon is black, the mean height of the soil surface above the zero level is greater and the forest-floor subtype is common mor.

The occurrence of the various forest-floor subtypes in relation to the various soil-texture categories and height classes is shown in Table 10. The association of forest-floor subtypes with height above the zero level is very pronounced and especially so where

TABLE 10

Frequency of occurrence of the various forest-floor subtypes in relation to soil texture and height of the soil surface above the zero level

Texture	1. Loamy sand					2. Fine sand					3. Coarse sand				
Forest-floor subtypes *	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Height-class															
12.	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
11.	–	–	–	–	–	–	–	1	2	–	–	–	–	1	–
10.	–	–	–	–	–	–	–	2	3	–	–	–	–	–	–
9.	–	–	–	–	–	–	–	1	3	–	–	–	–	–	2
8.	–	–	–	–	–	–	–	3	–	–	–	–	–	1	–
7.	–	–	1	–	–	1	7	3	1	–	–	–	1	–	1
6.	–	2	–	–	–	–	4	4	–	–	–	–	–	–	–
5.	5	–	–	–	–	1	2	4	–	–	–	–	–	–	–
4.	6	2	–	–	–	2	5	–	–	–	(1)	–	–	1	1
3.	2	1	–	–	–	3	2	1	–	–	(1)	–	–	–	1
2.	–	–	–	–	–	1	–	1	–	–	(1)	–	–	–	–

* Forest-floor subtypes: 1 = common mull, 2 = mull rich in litter, 3 = light mor, 4 = common mor, 5 = mor poor in humus.

(1) = free $CaCO_3$ present.

the soil is fine sand in texture. At the lowest heights above the zero level there is a strong tendency for mull to form on fine sand. With increasing altitude there is a steady shift towards the common-mor forest-floor subtype. The same tendency is found in loamy sand soils but not in the very coarse sand soils. The locally occurring, thick layer of very coarse sand has a very poor water-holding capacity and here the upper layer of soil does not benefit from a short distance to the water table and is much "dryer" than would seem to be the case from the height above the zero level, and here mor poor in humus is found. Since soil texture and height of the soil surface above the zero level are the main factors determining the soil–water relationships the formation of the various forest-floor subtypes might ultimately be determined by the latter.

It is difficult to judge whether different tree species will have different effects on the soil–water relationships due to different kinds of organic matter and humus being produced. It is however considered that this effect would not be very great.

Examination of Tables 9 and 10 indicates that in the case of an oak vegetation it is possible, from a knowledge of the soil texture of a site and its height above the zero level, to predict the forest-floor subtype, the colour of the upper part of the A_1-horizon

and the degree of leaching. The relationships are less clear with a vegetation of birch especially since the variation in the height of the soil surface above the zero level is rather small. If quadrats having soils of the same texture, *e.g.* fine sand, be considered then the degree of leaching is the only remaining variable characteristic.

The degree of leaching is largely determined by the intensity of the downward movement of water through the soil which in turn is determined by 1) the quantity of rainwater, 2) the porosity of the soil which is largely determined by the texture of the soil, 3) the distance to the water table, and 4) the rate of evaporation in the soil and the rate of loss of water vapour from the soil surface.

It is probable that, with the exception of porosity, these factors will not vary very much for the various quadrats carrying birch at Hackfort. It is also probable that water-containing substances produced in the process of decomposition of litter from the same type of vegetation will, in the case of the various sites, have the same capacity for leaching action on soil particles. Since the effect of a similar amount of leaching action will be less apparent in the case of a fine sand than with a coarse sand the data concerning texture, perhaps inadequately assessed in the field, might be more precisely evaluated by paying more attention to the degree of leaching. Therefore, if the degree of leaching as well as texture and height of the soil surface above the zero level is taken into consideration then it may be possible to predict the forest-floor subtypes and the colour of the upper part of the A_1-horizon of soils carrying birch.

Generally the degree of leaching is partly dependent on the height of the soil above the water table. In the lower lying parts of the Hackfort area the water table approaches to within 35 cm of the soil surface during part of the winter. The reaction of the ground water varies from pH 5.6 to pH 7.6. It is therefore quite possible that the upper parts of the soil will be enriched by mineral salts from the ground water thereby interfering with the leaching processes. In the places where there is a thick layer (30 to 60 cm) of coarse to very coarse sand, a slowing-up of the leaching processes cannot be detected and leaching is very strong. It is especially under these conditions that mor poor in humus occurs.

The soils developing on sites rich in lime have not received much consideration. The presence of free $CaCO_3$ in the A_1-layer

influences soil development so strongly that comparisons with acid soils are difficult. The precise manner in which lime influences the decomposition of plant debris and the formation of forest-floor subtypes requires closer investigation especially in relation to the accompanying water regime.

The water regime is a complex factor and still very difficult to evaluate quantitatively, particularly in relation to thin and often spongy soil layers such as occur in the A_1-horizons and the surface organic layers of the sites under consideration. The influence of the water regime on the differential development of mull and mor could only be considered indirectly through soil texture and height of the soil surface above the zero level.

The previously mentioned possibility of predicting the forest-floor subtype of an area, from data concerning soil texture and height of the soil surface above the zero level, was checked under the conditions occurring in the Hackfort area. A map showing the distribution of the heights of the soil surface above the zero level was superimposed on a map, showing the distribution of soils of different textures; the areas having similar categories of height class and texture were delimited. Since the various areas had been previously coded for the different categories of the various characteristics it was now possible to deduce the probable forest-floor subtypes (Fig. 5). Using this method it is only possible in some cases to classify an area as 3/4 or 1/2 for example; *i.e.* it is only possible to predict that the forest-floor subtype will be between light mor and common mor in the one case and between common mull and mull rich in litter in the other. Only field examination can resolve these cases where the existence of intermediate subtypes is indicated.

It never happened that the superimposed maps indicated the presence of transitional forms such as 1/5, 1/3 or 2/4; on the contrary in all cases the intermediate forest-floor subtypes lay between closely allied forest-floor subtypes. Bearing this in mind, the agreement between the predicted distribution of forest-floor subtypes (Fig. 5) and the distribution as determined in the field (Fig. 2) is remarkably good. It is therefore concluded that the formation of mull and mor under the conditions of the Hackfort area can be said to be strongly correlated with the two factors soil texture and height of the soil surface above the zero level.

From this it is considered that the soil water regime is the primary factor determining the differential development of mull and mor under the conditions of the Hackfort area.

Since this theory has been derived from observations in the Hackfort area alone, apart from evidence pointing in the same direction obtained from superficial investigation of two very different forests having soils chemically and structurally different, it must be checked by observations in other areas. Nevertheless the theory should be borne in mind in field soil surveys since the development of the various forest-floor subtypes and especially of the main forest-floor types mull and mor is closely related to the various processes of decomposition and transformation of organic matter. This applies to both forest soils and the soils associated with grass vegetations.

It might be possible that from the various humus characteristics of arable land, the forest-floor subtype which would develop there and the water regime present can be deduced; and *vice versa*, the forest-floor subtype of an area can give an indication of its properties for arable purposes.

SUMMARY

The distribution of mull and mor, in an area which is believed to have borne forest for a number of centuries at least, led to investigations into the reasons for their development.

Although the term forest-floor type has been substituted for humus type, mull and mor are used in the Müller-Hesselman sense.

There appeared to be no obvious relationship between the distribution of the various forest-floor subtypes and the results of chemical analyses and pH determinations on soil samples.

Where free $CaCO_3$ occurred in the A_1-horizon, a mull forest floor had developed even on coarse sand and the associated herb flora differed only slightly from that occurring on very acid mull. As the manner in which lime influences most soil processes is still unknown, the areas in which free $CaCO_3$ occurs were excluded from the investigations.

Assessments of various other soil characteristics were made and the frequency of association of the various categories of these characteristics ascertained.

It is concluded that the colour of the upper part of the A_1-horizon and its degree of leaching are related to its texture, and that the forest-floor subtypes are more closely related to soil texture than to soil colour or degree of leaching.

Each forest-floor subtype is associated with particular colouring of the upper part of the A_1-horizon and variation in both characteristics seems to be similarly associated with variations in topography.

There seems to be little demonstrable difference between the influence of the tree species oak and birch on the development of the forest-floor types.

The development of forest-floor types is closely related to the two factors soil texture and topography and it is considered that under the conditions of the Hackfort area the differential development of forest-floor types mull and mor and their subtypes is primarily determined by the soil water regime.

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EVALUATION OF LABORATORY INDEXES OF ABSORPTION OF SOIL PHOSPHORUS BY PLANTS: II *

by E. J. THOMPSON, A. L. F. OLIVEIRA, U. S. MOSER, and C. A. BLACK **

In the first paper in this series, Moser *et al.* [5] compared several laboratory indexes of the uptake of phosphorus by plants from samples of 22 soils. The samples were selected from different locations in the United States to represent a wide variety of soils. This approach was employed on the basis that the rigor of a test of general applicability of a given laboratory method should be greater if the group of samples employed in the test is heterogeneous than if it is homogeneous. Experience indicates that most, if not all, of the laboratory methods that have been proposed will give good results if the variation in properties of the soils is restricted sufficiently in respects other than the phosphorus supply. The present paper reports the results of a comparison of additional laboratory methods using the same group of soil samples.

METHODS

Extraction with ammonium fluoride, hydrochloric acid solution

Five-gram samples of air-dry soil in Erlenmeyer flasks were shaken by hand for 1 minute at room temperature with 35-ml quantities of a solution that was 0.03 *N* in NH_4F and 0.025 *N* in HCl. The suspensions were filtered immediately and analyzed for inorganic phosphorus by the method of Dickman and Bray [2]. The method described is essentially that recommended by Bray and Kurtz [1]. The modification was made that the aliquots

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of solution employed for the phosphorus determination were treated with 1 ml of a saturated solution of boric acid before the blue color was developed.

Extraction with citric acid solution

Five-gram samples of air-dry soil in Erlenmeyer flasks were shaken for 2 hours with 50-ml quantities of a 2% solution of citric acid. The flasks were allowed to stand for 24 hours and then were shaken again for 1 hour, after which a portion of the suspension was filtered. The extraction was carried out at room temperature. The total-phosphorus concentration of the filtrate was determined by the gravimetric method of Lorenz, as described by Piper [7] (pp. 150–153).

Extraction with lactate solution

Five-gram samples of soil in 400-ml bottles were shaken at room temperature for 2 hours with 250-ml quantities of lactate buffer solution, and enough of the suspension then was filtered to obtain 25-ml quantities of clear solution for the determination of inorganic phosphorus by the method of Dickman and Bray [2]. The lactate solution used for extraction was 0.02 N in Ca-lactate and 0.01 N in HCl and had a reaction of pH 3.5. The extractant and extraction procedure are those described by Egner [3] except that the extraction temperature was about 5°C higher than that employed by Egner.

Isotopic dilution

Five-gram samples of soil in 250-ml. Erlenmeyer flasks were shaken continuously for 24 hours at 24°C with 100-ml quantities of 1×10^{-4} M KH_2PO_4 solution containing P^{32}. A quantity of the suspension then was centrifuged. One aliquot of each of the clear solutions obtained by centrifuging was evaporated on an aluminum disk and counted with an end-window, Geiger-Müller counter and associated scaler. A total of about 10,000 counts was obtained with each sample. A second aliquot of each of the clear solutions was analyzed for inorganic phosphate by the method of Dickman and Bray [2]. Aliquots of the same volume of the original phosphate solution were counted and analyzed concurrently. The results were calculated by the equation

$$P_s = \frac{c_a k_f P_f}{c_f k_a} - P_a$$

where P_s = quantity of labile soil phosphorus that equilibrates with the P^{32}-tagged orthophosphate added, P_a = quantity of phosphorus added in the phosphate solution, P_f = quantity of phosphorus present in solution after equilibration with soil, c_a = counts of P^{32} per minute in aliquot fraction k_a of phosphate solution added, and c_f = counts of P^{32} per minute in aliquot fraction k_f of solution after equilibration with soil. By counting concurrently the same volumes of the solution added and the solution obtained from equilibration with soil, corrections were avoided for decay

of the isotope, for counter fluctuations from day to day, and for aliquot size ($k_f/k_a = 1$). The equation is developed on the assumption that equilibrium has been attained, hence it does not have exact significance in the present application where true equilibrium is not attained in a period of 24 hours. This method was described to the authors in a private communication from Dr. S. R. Olsen, U.S. Department of Agriculture, Ft. Collins, Colorado, as the technique he employed in isotopic-dilution measurements of labile soil phosphorus.

Percentage phosphorus saturation

The intent of the "percentage saturation" method is to determine the percentage of the "phosphorus adsorption capacity" that is occupied by phosphate. Two separate measurements are involved, namely, the phosphorus present and the "adsorption capacity" or "adsorption maximum".

The adsorption maximum was found by the method of Olsen and Watanabe [6]. Five-gram samples of air-dry soil in 250-ml Erlenmeyer flasks were shaken continuously for 24 hours at 24°C with 100-ml quantities of monobasic potassium phosphate solutions having the concentrations, 0.1, 0.2, 0.3, 0.5, 0.7, 0.9, and 1.2 millimoles per liter. All the phosphate solutions were adjusted initially to pH 7. After equilibration with the soil, the suspensions were centrifuged, and aliquots were analyzed for phosphorus by the method of Truog and Meyer [8]. The difference between the initial quantity of phosphorus in solution and the quantity present after equilibration was taken to be the quantity adsorbed. To calculate the adsorption maximum, the equation

$$\frac{c}{x/m} = \frac{1}{kb} + \frac{c}{b}$$

was employed. In this equation, proposed originally by Langmuir [4] for a different process, c is the molar concentration of phosphate in solution after equilibration, x is the quantity of phosphorus adsorbed by the mass m of soil, k is a parameter, and b is the adsorption maximum. The units of b are those of x/m. Where experimental data may be represented by the equation, a plot of $\frac{c}{x\ m}$ against c yields a straight line having the slope $1/b$ and the intercept $1/kb$. Since the soils contained some adsorbed phosphorus before equilibration with the phosphate solutions, this quantity was added to the quantity adsorbed from the phosphate solutions; *i.e.*, x = quantity of adsorbed phosphorus present initially in 5 g of soil + quantity of phosphorus adsorbed by 5 g of soil during equilibration with phosphate solution. The quantity of adsorbed phosphorus present initially was estimated by the labile soil phosphorus found by the method of isotopic dilution, described previously. Hence, the percentage saturation of the adsorption capacity by phosphorus is given by (labile soil phosphorus by isotopic dilution) (100)/(adsorption maximum, represented by b). With most of the soils, a plot of $c/(x/m)$ against c did not yield a straight line throughout the

entire range of concentrations. In estimating the slope, $1/b$, a line was fitted only to the lower concentrations where the plot approximated a straight line. In some instances, as few as three points were employed.

Successive extractions with water

Five-gram samples of air-dry soil in 50-ml centrifuge tubes were moistened with 2 ml of water. Then 35 ml of water were added from a burette, and the tubes were shaken continously for 1 hour at 24°C, after which the soil was centrifuged to the bottom and the supernatant solution was poured off. The soil immediately was resuspended in 35 ml of water, the tube was shaken and centrifuged as before, and the supernatant solution was poured off. This process was repeated until 15 successive extractions had been made. The extracts were analyzed individually for phosphorus by the method of Truog and Meyer [8].

Single extraction with water

One-gram samples of air-dry soil in 250-ml Erlenmeyer flasks were shaken for 15 hours at 24°C with 105 ml of water. A quantity of the suspension then was centrifuged, and the supernatant solution was analyzed for phosphorus by the method of Truog and Meyer [8].

RESULTS AND DISCUSSION

Table 1 gives the yields of phosphorus in sorghum plants grown on the soils in greenhouse cultures, together with measurements made on the soils by several laboratory methods. The yields of phosphorus and soil pH values are taken from the paper of Moser *et al.* [5]. The soil type names and the source of the samples are given in the same paper but are not repeated here.

Table 3 gives an evaluation of the various methods on the basis of the precision with which the yields of phosphorus may be estimated from the soil measurements in a linear regression of the former on the latter. The evaluation is expressed in the form of the probability of obtaining an F ratio for the regression as high as or higher than that found experimentally if the true regression were zero in the population of which the selected soils represent a sample. With a given number of independent variables used in the estimation, the lower is the probability, the greater is the precision. This technique is used in preference to a direct measure of precision, because probabilities may be compared directly among methods irrespective of the number of independent variables involved, whereas measurements of precision *per se* cannot.

TABLE 1

Phosphorus removed from soils by plants, and associated measurements on soils by laboratory methods								
Soil No.	Yield of P in plants per culture mg	Soil pH	Labile phosphorus in soil by indicated method, ppm				"Phosphorus adsorption capacity" of soil, ppm	"Percentage phosphorus saturation" of soil
			0.03*N* NH_4F, 0.025*N* HCl	Citric acid	Lactate buffer	Isotopic dilution		
F2814	18.1	6.75	30.3	174	27.3	71.5	268	27
F2815	5.5	5.69	1.2	309	1.5	−14.5	*	*
F2816	17.8	5.30	76.4	572	54.0	37.2	169	22
F2817	6.2	8.10	21.0	826	259.2	15.2	99	15
F2818	9.4	8.20	10.0	337	58.5	27.2	87	31
F2819	5.6	6.10	4.1	37	1.7	−8.5	658	−1
F2820	5.0	8.20	6.9	216	53.1	−3.2	75	−4
F2821	10.5	5.65	18.8	95	6.2	12.4	270	5
F2822	4.4	6.40	4.9	23	1.5	7.3	355	2
F2823	2.3	6.10	2.9	31	1.8	−9.1	375	−2
F2824	17.2	6.40	35.6	234	40.4	48.7	112	43
F2825	18.4	7.50	41.9	295	57.5	48.2	119	40
F2826	2.5	6.45	3.0	49	1.9	8.8	149	6
F2827	7.0	6.50	9.0	224	16.9	7.9	88	9
F2828	8.0	8.35	3.7	148	12.4	16.7	130	13
F2829	44.7	6.00	46.2	335	60.8	71.8	146	49
F2830	31.1	5.76	79.7	216	79.9	105.3	183	58
F2831	12.7	6.25	46.1	180	28.1	59.1	252	23
F2832	8.2	5.90	28.8	66	12.9	41.7	303	14
F2833	9.7	5.50	44.1	56	16.0	17.7	100	18
F2834	14.9	5.70	88.2	231	43.7	23.8	46	52
F2835	33.2	6.21	35.6	367	34.2	44.7	121	37

* The "phosphorus adsorption capacity" of this soil is relatively high, but it could not be calculated for the reason that a plot of $c'/(x/m)$ against c yielded a line with a slightly negative slope; this would result in a negative value for the phosphorus adsorption capacity. In the absence of a value for phosphorus adsorption capacity, the "percentage phosphorus saturation" could not be calculated.

Of the methods compared in Table 3, the lowest probabilities are associated with the methods of water extraction, isotopic dilution, and "percentage phosphorus saturation". These methods provide the most precise estimation of the yields of phosphorus. The highest probabilities are associated with the methods of extraction with citric acid and lactate buffer. These methods provide the least precise estimation.

The poor results with citric acid can be attributed principally to eight soils. With six, the quantity of phosphorus extracted is relatively high in relation to the yield of phosphorus. Three of these are alkaline (F2817, F2818, and F2820). Citric acid of course would dissolve considerable apatite-type phosphate of low availa-

TABLE 2

Cumulative amounts of phosphorus removed from soils by successive extractions with water and by a single extraction with water

Soil No.	Phosphorus extracted, ppm of soil															
	Cumulative amount in indicated number of successive extractions at soil-to-water ratio of 1 to 7															Quantity in single extraction at soil-to-water ratio of 1 to 105
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
F2814	1.2	2.5	3.4	4.3	5.1	5.9	7.0	8.1	9.1	10.0	10.9	11.7	12.5	13.4	14.4	22.1
F2815	0.2	0.3	0.3	0.4	0.5	0.6	0.7	0.7	0.8	0.9	1.0	1.1	1.2	1.2	1.4	2.6
F2816	1.9	3.7	5.5	7.2	9.0	10.8	12.4	13.9	15.3	16.7	18.1	19.4	20.6	21.6	23.0	21.7
F2817	1.4	3.9	6.7	9.1	11.0	12.5	14.5	16.6	18.3	19.7	21.4	23.0	24.8	27.1	29.4	14.9
F2818	2.5	5.0	7.2	9.3	11.0	12.8	14.2	15.8	17.4	18.7	19.9	21.2	22.4	23.4	24.7	26.0
F2819	0.1	0.1	0.2	0.2	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.8	0.8	0.9	4.2
F2820	0.6	1.6	2.4	3.3	3.8	4.5	5.0	5.5	5.9	6.4	6.8	7.1	7.5	7.7	8.2	10.5
F2821	0.1	0.3	0.6	0.9	1.2	1.6	2.0	2.6	3.0	3.3	3.7	4.1	4.6	4.9	5.3	4.2
F2822	0.2	0.2	0.3	0.5	0.6	0.7	0.9	1.1	1.2	1.3	1.4	1.6	1.7	1.8	2.1	4.4
F2823	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.6	0.7	2.0
F2824	3.9	8.6	12.6	15.7	18.3	20.8	23.1	25.1	26.8	28.3	29.6	31.0	32.2	33.4	34.6	29.1
F2825	3.5	8.1	12.3	15.5	18.2	20.9	23.5	25.7	27.4	29.4	31.1	32.7	34.0	35.4	36.8	27.4
F2826	0.1	0.2	0.4	0.6	0.9	1.2	1.5	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.7
F2827	0.3	0.9	1.7	2.4	2.9	3.4	4.0	4.5	5.0	5.4	5.8	6.2	6.6	6.9	7.3	10.4
F2828	0.2	0.9	1.8	2.6	3.4	4.2	5.0	5.6	6.3	7.0	7.7	8.4	9.0	9.6	10.3	9.2
F2829	5.9	11.9	16.6	20.8	24.1	27.2	30.1	32.8	35.0	37.3	39.3	41.2	43.1	44.6	46.4	34.1
F2830	8.6	14.6	18.8	22.2	25.2	28.6	32.0	35.0	37.9	40.9	43.9	46.6	49.6	52.1	54.9	41.6
F2831	0.2	0.7	1.3	1.8	2.5	3.1	3.7	4.3	4.9	5.5	6.2	6.8	7.3	7.8	8.5	20.2
F2832	0.1	0.3	0.4	0.5	0.7	0.9	1.0	1.2	1.4	1.6	1.8	1.9	2.1	2.3	2.6	9.2
F2833	0.4	1.5	2.5	3.4	4.3	4.9	5.7	6.5	7.2	7.8	8.5	9.2	9.8	10.4	11.1	13.8
F2834	4.8	8.3	11.1	13.6	16.0	18.6	20.4	22.6	24.4	26.3	28.1	30.0	31.6	33.3	34.8	25.3
F2835	2.0	5.0	7.8	10.5	13.0	15.2	17.2	18.8	20.5	21.9	23.2	24.5	25.6	26.7	27.9	19.8

TABLE 3

Probability of obtaining an F ratio as high as or higher than that found experimentally for the linear regression of yield of phosphorus in sorghum plants in greenhouse cultures on the phosphorus measurement on corresponding samples of soil by various laboratory methods

Method	Probability
0.03N NH_4F, 0.025N HCl	2.4×10^{-3}
Citric acid	2.1×10^{-1}
Lactate buffer	5.9×10^{-1}
Isotopic dilution	1.5×10^{-5}
"Phosphorus adsorption capacity"	2.8×10^{-1}
"Percentage phosphorus saturation"	5.4×10^{-5}*
Cumulative amount of phosphorus removed in indicated number of consecutive extractions by water at soil-to-water ratio of 1 to 7	
1	4.1×10^{-5}
2	1.0×10^{-5}
3	9.1×10^{-6}
4	7.3×10^{-6}
5	5.9×10^{-6}
6	5.9×10^{-6}
7	5.6×10^{-6}
8	6.3×10^{-6}
9	6.3×10^{-6}
10	6.7×10^{-6}
11	7.1×10^{-6}
12	7.9×10^{-6}
13	8.6×10^{-6}
14	1.1×10^{-5}
15	1.3×10^{-5}
Phosphorus removed in single extraction by water at soil-to-water ratio of 1 to 105	1.4×10^{-5}

* The probability value is 2.4×10^{-4} where the regression is represented by a quadratic equation of the form $y = a + bx + cx^2$.

bility if such were present in alkaline soils. The remaining three are acid (F2815, F2816, and F2827), and one of these (F2815) is notable as a high-iron, phosphorus-fixing soil. Citric acid may be expected to extract unduly large amounts of phosphorus if present in such soils by forming soluble chelates with iron that is combined with phosphate. With two soils (F2829 and F2830), the ratio of yield of phosphorus in the plants to that extracted with citric acid is relatively high. These soils produced two of the highest yields of phosphorus and yielded more phosphorus to extraction with water than any other soils (Table 2). The quantities of phosphorus extracted from the soils are greater with citric acid than with any

of the other reagents or with plants, and this may have been one reason for the relatively poor performance. In general, one may expect that if a group of soils is subjected to an increasing degree of extraction with a given reagent, the amounts of phosphorus extracted will change progressively from an index of quality (and perhaps also of the effect of other soil constituents) to one of quantity of phosphorus in forms subject to extraction.

The poor performance of the lactate buffer method can be attributed principally to five soils. In three of these (F2817, F2818, and F2820), the quantity of phosphorus extracted by the reagent is relatively high per unit of phosphorus extracted by the plants. All three of these soils are alkaline and are the same ones that gave a similar type of deviation with the citric acid method. The cause of the deviation probably is the same, namely, extraction of apatite-type phosphates of low availability by the acid reagent. Lactate does not have the chelating properties of citrate, and perhaps for this reason does not extract unduly large quantities of phosphorus from the three acid soils (F2815, F2816, F2827) that are out of line with the citric acid method. With two soils (F2829 and F2835), the ratio of yield of phosphorus in the plants to phosphorus extracted by the lactate buffer is relatively high. These two soils almost invariably deviate in the same direction, irrespective of the method. Since the methods are rather dissimilar, it appears that the cause of the deviation lies principally with the value for yield of phosphorus and not with the soil measurements.

The precision of estimation obtained with the 0.03*N* NH_4F, 0.025*N* HCl method is greater than that obtained with the citric acid and lactate buffer methods. The three alkaline soils that give aberrant results with the citric acid and lactate methods are not out of line with the 0.03*N* NH_4F, 0.025*N* HCl method. Only two soils (F2829 and F2835) are definitely out of line with the 0.03*N* NH_4F, 0.025*N* HCl method, and these are the two that deviate almost invariably, as mentioned in the preceding paragraph. One additional point that should be mentioned with respect to the 0.03*N* NH_4F, 0.025*N* HCl method is that the performance probably is biased downward as a result of the method of selecting the samples. The sampling sites were selected, on the basis of previous field experiments, to provide a group of samples on which the performance of the 0.03*N* NH_4F, 0.025*N* HCl method was poor. If

some other basis for selection had been employed, therefore, the precision of prediction obtained with the 0.03N NH_4F, 0.025N HCl method would be expected to be improved relative to that of the other methods.

The precision of estimation of yields of phosphorus in the plants from the labile phosphorus by isotopic dilution is better than that from the phosphorus extraction methods discussed thus far. Only soils F2829 and F2835 are definitely out of line with the trend exhibited by the other samples.

Evaluation of the "percentage phosphorus saturation" method presents a problem somewhat different from the methods discussed previously. A plot of yield of phosphorus against percentage phosphorus saturation is concave upward. The principal cause of this trend is the results with soils F2829 and F2835, the aberrant behavior of which was discussed previously. Nevertheless, a slight tendency for the plot to be concave upward exists in the remaining data. While it does not seem reasonable that this trend would continue at phosphorus-saturation percentages much higher than those encountered, the present state of knowledge does not permit rejection of a curve that is concave upward within the range of values encountered. Hence two probabilities are given in Table 2 for the percentage phosphorus saturation method. One is for the linear regression (in which the data for soils F2829 and F2835 are out of line with the other results), and one is for the curvilinear regression. The former appears to be the better evaluation. This investigation demonstrates no advantage of percentage phosphorus saturation over labile phosphorus by isotopic dilution as an index of the uptake of phosphorus by plants.

Since they may be of some interest, the values for "phosphorus adsorption capacity" obtained in the process of deriving the "percentage phosphorus saturation" are included in Table 1. There is a tendency for low yields of phosphorus to be associated with a high phosphorus adsorption capacity, as might be expected. Hence, the adsorption-capacity data are of some value in estimating the yields of phosphorus. The probability value for phosphorus adsorption capacity is 2.8×10^{-1}.

The experimental data obtained from the extractions with water are given in Table 2, and the probabilities are given in Table 3. Extraction with water proved to be the best of the methods em-

ployed in this work. The probabilities are equal to or lower than those obtained previously on the same samples by Moser *et al.*[5] by the method of extraction with an anion-exchange resin. Sample calculations of H_2PO_4 and HPO_4 were made on the cumulative amounts of phosphorus in seven extractions to see whether the precision of estimation would increase as Moser *et al.* found to be the case with the resin method. In making the calculations, the measurements of pH in water were employed, and the ionic strength was assumed to be equivalent to that of 0.001*M* $CaCl_2$. The probability value obtained was 3×10^{-7}, which is lower than the value 5.6×10^{-6} obtained for the total phosphorus removed in seven extractions, and which compares favorably with the value of 2×10^{-7} obtained by Moser *et al.* for the same group of samples. The method of extraction with water thus appears to be a promising one for practical use, because the technique of water extraction is simpler than that of extraction with an anion-exchange resin. The method of successive extractions employed in this research, of course, is not suitable for practical application.

The probability value for phosphorus removed in a single extraction using a 1-to-105 ratio of soil to water is about the same as that for 15 consecutive extractions (where the total ratio of soil to water is the same, *i.e.*, $15 \times 7 = 105$). A plot of the data, however, shows that except for the usual two aberrant soils (F2829 and F2835), the scatter of points is less with the single extraction using a 1-to-105 ratio than with the 15 consecutive extractions or, in fact, with any number of consecutive extractions. Hence the indications are that with further investigation the method of extraction with water can be developed to provide estimates of phosphorus uptake by plants that are relatively precise and at the same time convenient to obtain.

SUMMARY

A comparison was made of several laboratory methods for estimating the yield of phosphorus in plants grown in greenhouse cultures on samples of 22 soils from different parts of the United States. The methods investigated and their rank in order of increasing precision of the estimates of the yield of phosphorus were as follows: extraction with lactic acid, calcium lactate buffer solution = extraction with 2 per cent citric acid solution = extraction with 0.03 *N* NH_4F, 0.025 *N* HCl solution < "percentage phosphorus

saturation" found as follows: 100 × labile phosphorus by isotopic dilution ÷ "phosphorus adsorption capacity" according to Langmuir adsorption equation) ≤ labile phosphorus by isotopic dilution ≤ phosphorus extracted by water.

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PRINCIPLES AND PROBLEMS OF THE CHEMICAL ESTIMATION OF THE SUPPLY OF AVAILABLE SOIL MANGANESE

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1. INTRODUCTION

Ever since several workers got yield increases with manganese fertilizers at the beginning of the 20th century and since McHargue [23] in 1919 first established that manganese is an essential nutrient for wheat, there has been a growing interest in the estimation of available soil manganese. This interest was stimulated by the increasing occurrence of manganese-deficiency symptoms of important crops often due to overliming in course of the necessary process of liming of acid soils and intensified by the yield increases due to the application of major-nutrient fertilizers.

The first methods of assessing the available soil manganese have been developed in Australia by Piper [27] and Leeper [20], and in Denmark by Steenbjerg [31]. Most of the further work in this line up to the present can be described as modifications of these basic suggestions. The hardly disputable fact that the development of successful methods is still far from being complete may serve as an excuse for the following exposition. Naturally this short review of the principles and problems involved in the estimation of what is commonly called 'available manganese' in the soil cannot give a bibliography of all attemps made.

From the viewpoint of plant nutrition the Mn-status of the soil, like that of other nutrients, is an important subject of study. There is especially a need for the prediction of the supply of available manganese by means of chemical or biochemical methods. The degree of supply of available manganese of a soil depends on

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the concentration of available manganese and on the rate of its release from the so-called reserve. The difficulty of interpretation of the term 'available' shall be disregarded in this context. 'Available manganese' here simply means the more soluble portion of the total soil manganese that can be taken up by active plant roots. From this common definition it follows that methods of assessing available manganese (or other nutrients, of course) are strictly only valid for the plant variety used, for the soil tested and for the special conditions of plant growth. In addition, due to the complex nature of the soil and the soil—plant relationship it is evident that the methods developed are necessarily empirical.

2. DEVELOPMENT OF METHODS

Methods for the estimation of the supply of available soil manganese can be obtained in different ways, namely (1) by determining a certain fraction of the soil Mn, (2) by using another soil factor highly associated with the available Mn, and (3) by determining several factors which regulate the supply of available Mn.

2.1. *Methods based of the determination of a Mn-fraction*

The first possibility which is mainly applied is the determination of a certain Mn-fraction. This fraction is supposed to represent the amount of available Mn. This line of investigation might be called the 'search for the ideal extractant' (Peech [26]). It involves, as close as possible, an imitation of the plant mechanism for Mn-uptake, although the ultimate goal can hardly be reached (Piper [28]). The basis of these studies therefore is the knowledge of the forms of Mn in the soil on the one side (Leeper [21], Heintze [14]) and of the plant mechanism of acquiring Mn on the other. Many chemical and biological extractants for Mn-fractions have been devised, mainly for the water-soluble, the exchangeable, the acid-soluble, the reducible and the complex-bound manganese (for description see: Jackson [16]). Most methods are not restricted entirely to only one of these fractions.

The main difficulty of determining a certain Mn-fraction supposed to be representative for the available Mn consists in the fact that the different forms of Mn in the soil have an unequal degree of availability. For example, the widely used fraction of 'active

Mn' consists of three subfractions of a very different level of accessibility to the plant, *i.e.* the very easily obtainable soluble Mn, the readily available exchangeable and the easily reducible Mn, the latter being more a measure of the potential supply over a given period (Boken [3]). On certain soils, however, some of these subfractions mentioned may be present only in negligible amounts and need not be considered.

It seems likely that the plants absorb Mn^{++}-ions mainly from the soil solution and from the sorption complex and that therefore these fractions are most suitable for representing the available Mn. But unfortunately these values are very inconstant in the soil (Fujimoto and Sherman [9], Christensen, Toth and Bear [5], Kosegarten [19]), and from this point of view are not very suitable values for methods used in practice, although this difficulty may be partly overcome (Boken [2]).

2.2. *Methods based on another factor than a Mn-fraction*

The second possibility, more recently developed, is the use of factors that influence the Mn-status or are at least highly associated with it. Considering also that Mn-fractions are actually only measures of the degree of supply of available Mn it seems to be promising to indicate the Mn-status by easily determinable and more constant factors influencing the Mn-supply.

Well-known examples are the use of the pH-value as an indicator of available Mn in podzols, a fact well established by several workers, and that of the C N ratio in estuary soils (de Groot [11]). The pH value influences and is highly associated with the exchangeable Mn, a fact known from field investigations of many workers (Mattson [22], Heintze [13], Schachtschabel [30]) and expected from theoretical considerations (Jarilova [17], Eriksson [6]). The C N ratio seems to effect its influence via the oxidation—reduction potential.

2.3. *Methods based on several factors*

The third possibility, only very recently applied, is the use of several factors. Looking back, this development seems quite natural because the degree of supply of available soil Mn is actually influenced by several factors: mainly by the content of moderate soluble Mn-reserves, by the pH value and the oxidation—reduction

potential, by organic matter content, *etc.* Despite preliminary suggestions (Finck [7], Jones [18]) it was Rich [29] who first developed this new line.

The main advantage of the use of several factors consists in the fact that one can take Mn-fractions as well as other suitable factors and that one can avoid factors which show a great seasonal or even daily variation and restrict oneself rather to more or less constant soil data. Last, but not least, it should be possible to reach a higher degree of association with the plant-available Mn by means of the multiple correlation of several factors than with a single one. However, the expense of analytical work limits the number of factors which can be determined.

3. EVALUATION OF METHODS

A chemical or biochemical method for the determination of available nutrients normally consists ot two parts, namely that of a suitable extractant and that of a procedure for the determination of the nutrient extracted. The value of a method depends mainly on the suitability of the extractant. Therefore an evaluation becomes necessary. The evaluation of methods is of such importance that even apparently brilliant and logical suggestions of new extractants without any evaluation or with only a very superficial one are hardly worth mentioning as new methods. It will be useful in this connection to keep in mind the remark of Beveridge [1] that 'logical reasoning is quite unreliable as a guide to the truth in biological research'. This apparently holds true for all research topics of a complex nature.

Evaluation implies calibration by means of a suitable standard. The value of a method depends on the quality of the standard and on the degree of association obtained with the standard selected.

3.1. *Standards for calibration*

For the calibration of Mn-methods there are three main standards available: (1) plant yields, (2) plant Mn-contents and (3) Mn deficiency symptoms.

3.1.1. Plant yields as a standard. Obviously the best standard would be a scale of plant yields from field experiments due to

differences in Mn-supply of the soil, but in comparison with the major nutrients (Bray [4]) the possibility of obtaining such data for Mn is very limited. The main reason for this failure seems to be the non-uniformity of the Mn-supply of the soil particularly within the marginal area of the deficiency which makes it difficult to carry out reliable experiments.

One might assume that this difficulty could be overcome by using pot experiments, but this procedure unfortunately does not reflect field conditions very well, a fact especially important in respect of the moisture status which strongly influences the Mn-availability.

3.1.2. Mn-content of plants as a standard. Considering the difficulties in taking yields as a standard, the standard mostly used at present is the Mn-content of plants, strictly speaking, the concentration of total Mn within certain parts of the plant at a certain stage of growth. The application of this relatively easily obtainable standard is possible because (quite different, for example, from the case of iron) the concentration of total Mn normally is highly associated with that of 'mobile or active' Mn in the plant. However, there are exceptions under extreme conditions (Mehlich [24]).

Despite its unequal distribution the Mn-concentration in the plant as a ratio of actual amount of Mn and total plant mass naturally depends on all factors influencing the plant mass. From this point of view it may seem to be more promising to take the amount of Mn in the plant instead of the concentration. That, however, requires the estimation of the plant mass and leads to difficulties at least in those cases, where the distribution of Mn in leaves, stems, *etc.* is very unequal. It has usually been preferred to use as a standard the Mn-concentration of the dry substance of the leaves. The difficulty arising from the dilution effect caused by other factors is overcome by restriction of the sampling to a certain period of growth where the plants under comparison have almost equal or at least similar plant masses. As test plants, the most suitable are those which are most susceptible to Mn-deficiency, because they best indicate the Mn-supply of the soil. Such plants hitherto used are for example, oats, beets, some legumes such as groundnuts and soyabeans.

Considering the different possibilities of sampling it is clear that the Mn-contents of plants represent more a group of standards than a definite one. Therefore, in order to make comparisons between the results obtained in different parts of the world more fruitful, for future work some kind of agreement seems to be necessary which one might describe as a standardization of standards, *i.e.* to agree on the parts of plants to be taken or on the most suitable stage of growth.

The use of plant contents as a standard requires the establishment of a scheme of limiting values. For oats early in the growing season Mn-contents of 15 to 20 ppm are, according to several workers, the limit for the appearance of visual deficiency symptoms, while values above 30 to 40 ppm indicate an optimum supply (Nicholas and Fisher [25]). Goodall [10] reports a similar figure for wheat. Between these two limiting values lies the range of the latent deficiency.

3.1.3. Deficiency symptoms as a standard. The third standard of importance is the appearance of deficiency symptoms, mostly used in the alternative forms – deficient or not deficient. This standard is the easiest one to obtain, a fact that explains its widespread application. Besides the difficulty (negligible for some test plants) of distinguishing between Mn-deficiency and similar symptoms of another kind, the nature of this standard involves the disadvantage of differentiating merely between the apparent deficiency on the one side and the quite heterogeneous group of latent deficiency and adequate supply on the other side – thus providing no full-scale standard. However, in spite of this disadvantage this standard may serve some useful purpose.

3.2. *Association with the standard*

Whatever standard one chooses there will be the necessity of indicating the degree of association with the standard selected. It seems generally accepted that the application of regression and correlation statistics serves well for this purpose. Although the degree of association of the independent variables with the dependent one is frequently characterized by means of the correlation coefficient (r-value), the use of the coefficient of determination (r^2-value, commonly expressed in %) in combination with the regression data

might be preferable. The degree of association can be calculated not only in the case of a full-scale ordinate, but also where the *y*-axis consists of one alternative only, for example, deficient or not deficient.

In order to achieve a linear relationship between single soil values and the standard, a transformation of one variable (normally the dependent) may become necessary, usually a logarithmic one. This holds true especially for soils where the pH value is related to the Mn-uptake (Rich [29], Finck [8]). For neutral soils on the other hand the relation between (for example) active Mn and plant Mn is fairly linear (de Groot and Finck [12]), and the same seems to be valid if values of different soil types are considered simultaneously (Hoff and Mederski [15]).

SUMMARY

The principles and problems involved in the estimation of the supply of available soil manganese are summarized. Methods have been developed mostly on the basis of a single manganese fraction, but more recently there have also been suggestions of using other single factors or even several factors influencing the supply of available manganese. More important than the suggestion of an extractant is the evaluation of a new method, *i.e.* the calibration by means of a suitable standard.

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EVALUATION OF DRY-SUBSURFACE AND WET-SURFACE AMMONIUM SULFATE APPLICATION FOR RICE

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INTRODUCTION

In Egypt the total area under rice in the season ranges between 400 and 800 thousands feddans *, depending upon the amount of Nile water available for irrigation each year. Nitrogen is by far the most important fertilizer influencing rice yield and ammonium sulfate is widely used. The ammonium sulfate is usually applied broadcast on the surface of the wet soil.

The question of the best method of ammonium sulfate application for rice has received much attention in recent years. The work of Pearsall [5] on oxidation reduction zones in waterlogged soils indicated that the flooded rice soil develops two distinct zones in respect to nitrogen transformation. The upper thin layer in contact with water is oxidizing. Immediately beneath this oxidizing layer, there is a zone where reducing conditions prevail. When ammonium sulfate is broadcast on the oxidizing surface, the ammonium is partly absorbed by the rice plant and the rest is converted to nitrate which moves down with percolating water. In the lower reducing zone, the nitrate is reduced to nitrite and thence to atmospheric nitrogen which is lost. On the other hand, if ammonium sulfate is applied into the lower zone, the ammonium nitrogen remains unchanged and is available for rice.

Many experiments have been conducted for testing the surface and subsurface ammonium sulfate applications with considerable

* A feddan is equivalent to 4200.8 square meters.

variation in results [3 4 6]. Drilling ammonium sulfate in the seedbed before flooding increased rice yields from 25 to 50 per cent over the broadcast application [4]. Elhak [3] reported increases in rice yields ranging from 1 to 19 per cent for ammonium sulfate ploughed into the soil prior to flooding over the broadcast application.

Relative yield increases, however, are unsuitable for evaluating the two methods of application. The apparent yield increases change with the quantities of ammonium sulfate applied because yield responses are not a linear function of available nitrogen. On the other hand, a reliable evaluation of the two methods of application may be obtained by applying the availability concept of Black and Scott [2]. The concept was used by the authors to evaluate different fertilizer sources of a common nutrient. The availability was defined as the effective quantity and it is the product of the quantity and the availability coefficient. Absolute values cannot be assigned to availability coefficients or availabilities. However, the ratio of the availability coefficient of a nutrient in one fertilizer to that of the same nutrient in another fertilizer can be determined from appropriate response curves obtained from application of the fertilizers under comparable conditions.

In this study, the availability concept was extended to the evaluation of the surface and subsurface applications of ammonium sulfate. Nitrogen recovery by rice grain from the added fertilizer was also investigated.

EXPERIMENTAL

The experiment was conducted during the summer of 1958 to determine the effect of rate and method of ammonium sulfate application on yield response and nitrogen content of the rice grain. Plots were established at the Zahra farm of the Ministery of Land Reform near the city of Damanhour. Soil at this location is heavy clay of low permeability and slightly saline.

The statistical design was a split plot with the two methods of ammonium sulfate application as the main treatments, and these were replicated 4 times. Each of the main plots was split into 5 subplots on which there were 5 rates of nitrogen: 0, 10, 20, 30, and 40 kg per feddan added as ammonium sulfate. The plots were 20 meters long and 10 meters wide. Montakhab 147 rice was transplanted on June 10. All plots received a basic treatment of 150 kg of superphosphate and 25 kg of potassium sulfate per feddan before transplanting.

The two methods of ammonium sulfate application were the "dry sub-

surface" application and the "wet surface" application. In the dry subsurface application, ammonium sulfate was ploughed into the soil prior to flooding and transplanting. In the wet surface application, half of the ammonium sulfate was broadcast at tillering and the other half before heading. Each individual plot was harvested and a small thresher was used. Total nitrogen content of the grain was measured by the Kjeldahl method.

RESULTS

The effect of increasing amounts of ammonium sulfate upon the yield of rice in relation to the method of application is presented in Table 1. With both methods of application, a response to

TABLE 1

Yield of rice grain in kilograms per feddan in relation to rates and methods of ammonium sulfate application

Nitrogen applied, kg per feddan	Dry-subsurface application		Wet-surface application	
	Observed	Calculated	Observed	Calculated
0	2260	2260	2310	2260
10	2565	2581	2420	2452
20	2780	2771	2615	2598
30	2875	2883	2670	2707
40	2940	2950	2830	2790

nitrogen was obtained and the efficiency of nitrogen utilization decreased with increasing rates of ammonium sulfate. However, rice yields were consistently higher in case of the dry subsurface application. The results of the analysis of variance of the experiment are shown in Table 2.

TABLE 2

Analysis of variance

Source of variation	Degrees of freedom	Sum of squares	Mean square
Main plots:			
Methods of application	1	331	331
Blocks	2	214	71.33
Main plot error	2	65	32.67
Subplots:			
Rates of application	4	4555	1138.75
Rate × method	4	194	48.50
Subplot error	24	943	39.29
For methods of application: F = 331/32.67 = 10.13			
For rates of nitrogen: F = 1138.75/39.29 = 28.98			
Rate × method: F = 48.50/39.29 = 1.23			

It can be seen that the F value for "methods of application" is significant at the 5% level, and the F value for "rates of application" is significant at the 1% level. The evidence thus indicates that the dry-subsurface application was better than the wet-surface application. The significant differences among rates of ammonium sulfate application were not unexpected. Further, no interaction is indicated between rate and method of ammonium sulfate application.

Results of nitrogen analyses of rice grain did not indicate significant differences in the nitrogen content from plots receiving different ammonium sulfate treatments. The average nitrogen content of rice grain from all plots was 1.19 per cent.

DISCUSSION

The availability concept of Black and Scott [2] was applied to evaluate the two methods of ammonium sulfate application. According to this concept, differences in the response curves obtained with the two methods of application are attributed to differences in the effective quantities of nitrogen supplied by ammonium sulfate in each case. In other words, the higher yields obtained with the dry-subsurface application are due to the greater effective quantities involved. When adding a certain amount of ammonium sulfate to the soil, the effective quantity of nitrogen supplied by the dry-subsurface application is always greater than that supplied by the wet-surface application. This effective quantity of nitrogen may be represented as the product of the absolute quantity multiplied by an efficiency factor. With each method of application, the efficiency factor is constant for all levels of response. Therefore, the ratio of the efficiency factor of nitrogen in the wet-surface application to that in the dry-subsurface application is an estimate of the efficiency of the former method of application to the latter.

The response of rice to different rates of ammonium sulfate may be presented by the following form of the Mitscherlich equation:

$$y = A(1 - 10^{-c(x+b)})$$

where A is the maximum yield obtainable by increasing the rate of application x of ammonium-form nitrogen indefinitely, b is the nitrogen supplied by the soil measured in the same units as x, and

c is the efficiency factor. The two methods of ammonium sulfate application produce the same response y_0 when $x = 0$, and the same maximum yield A. They would differ, however, with respect to c, which determines the rate at which the response approaches the maximum yield A.

The two concurrent Mitscherlich curves were fitted by the least-squares method as described by White *et al.* [7] as follows:

$$y = 3045(1 - 10^{-0.0224(x+26.28)})$$

for the dry-subsurface application and

$$y = 3045(1 - 10^{-0.0122(x+48.24)})$$

for the wet-surface application.

Rice yields calculated from the above equations, Table 1, show satisfactory agreement with the observed values. The efficiency factors for the dry-subsurface and the wet-surface applications are 0.0224 and 0.0122 respectively. Therefore, the efficiency of the wet-surface application expressed as a fraction of the dry-subsurface application is 0.0122/0.0224 = 0.545.

The validity of the assumed model of two concurrent Mitscherlich curves was investigated by the analysis of variance shown in Table 3.

TABLE 3

Analysis of variance to investigate the assumed model of two concurrent Mitscherlich curves

Source of variation	Degrees of freedom	Sum of squares	Mean square
Replicates	3	214	
Treatments	9	5080	564.5
Regression	3	4187.2	1395.7
Residual	6	892.8	148.8
Error	27	1041	38.6
Total	39	6335	

For regression: $F = 1395.7/38.6 = 36.16$

For residual: $F = 148.8/38.6 = 3.85$

The minimum sum of squares obtained by the least-residues procedure [7] was 223.2. Since there were 4 replicates, the residual sum of squares not accounted for by regression is $4 \times 223.2 = 892.8$. The sum of squares attributable to regression is the difference between the residual sum of squares and the treatments sum of

squares. The degree of freedom for treatments were subdivided into "regression" and "residual" by assigning one degree of freedom to each parameter fitted. The F value of 36.16 for "regression" is highly significant, since a F value of only 4.60 is needed at the 1% level. The F value for "residual" is 3.85 which is slightly higher than 3.56, the value required for significance at the 1% level. The evidence thus indicates that the assumed model may be considered as satisfactorily characterizing the data. There is the possibility, however, that another functional model may provide a better fit, but the Mitscherlich equation was applied because of the interpretations that could be inferred from its parameters.

A further indication of the lower efficiency of nitrogen utilization in the wet-surface application is given by calculating the recovery of added nitrogen by rice grain. Calculations were made on the assumption that rice plants absorb soil nitrogen and fertilizer nitrogen in the same ratio as the respective availabilities. Soil nitrogen was estimated by the parameter b of the Mitscherlich equation in terms of the fertilizer nitrogen x. Therefore, the nitrogen in the grain taken up from the fertilizer is proportional to $x/(x+b)$. Balba and Haley [1] demonstrated, in case of phosphorus, that results obtained by this method of calculation were in close agreement with those obtained by radioactive measurements. Values obtained for nitrogen uptake from the fertilizer and percentage recovery of the added nitrogen by rice grain, for both methods of application, are recorded in Table 4. The percentage recovery of added nitrogen was estimated by

$$N/(x+b) \times 100$$

where N is the total nitrogen content of grain.

TABLE 4

Nitrogen uptake and percentage recovery by rice grain from added nitrogen in relation to rates and methods of ammonium sulfate application

Nitrogen applied, kg per feddan	Nitrogen uptake from fertilizer, kg per feddan		Recovery of added nitrogen %	
	Dry subsurface	Wet surface	Dry subsurface	Wet surface
10	8.41	4.94	84.1	49.4
20	14.30	9.12	71.5	45.6
30	18.23	12.18	60.8	40.6
40	21.12	15.27	52.8	38.2

The efficiency of added nitrogen generally decreased with increasing rates of nitrogen application. However, the recovery was fairly good with the dry-subsurface application. It was 84.1 per cent where 10 kg of nitrogen were applied per feddan and decreased to 52.8 per cent where the rate of nitrogen application was 40 kg per feddan. In case of the wet-surface application recoveries was considerably lower, 49.4 per cent, where 10 kg of nitrogen were applied per feddan and decreased to 38.2 per cent where the rate of nitrogen application was 40 kg per feddan.

SUMMARY

A split-plot design experiment was established in the Zahra farm near Damanhour to determine the effect of rate and method of ammonium sulfate application on yield response and nitrogen content of the rice grain. Ammonium sulfate applications supplied 0, 10, 20, 30, and 40 kg of ammonium-form nitrogen per feddan. In the dry-subsurface application, ammonium sulfate was ploughed into the soil prior to flooding and transplanting. In the wet-surface application, half of the ammonium sulfate was broadcast at tillering and the other half before heading.

With both methods of application, a response to nitrogen was obtained and the efficiency of nitrogen utilization decreased with increasing rates of ammonium sulfate. However, rice yields were consistently higher with the dry-subsurface application. Differences in the nitrogen content of rice grain from plots receiving different ammonium sulfate treatments were insignificant. The average nitrogen content of rice grain from all plots was 1.19%.

Yield response to different rates of ammonium sulfate for both methods of application, was presented by two concurrent Mitscherlich curves. The efficiency factors for the dry-subsurface and the wet-surface applications were 0.0224 and 0.0122 respectively. The value of 0.545 was obtained by expressing the efficiency of the wet-surface application as a fraction of the dry-subsurface application.

Nitrogen recoveries from the added fertilizer were considerably higher in the dry-subsurface application. Recoveries were 84.1 and 52.8 per cent in case of the dry-subsurface application, and 49.4 and 38.2 per cent with the wet-surface application where 10 and 40 kg of nitrogen were applied per feddan respectively.

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CATION EXCHANGE PROPERTIES AND PECTIN CONTENT OF STORAGE-TISSUE DISKS

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INTRODUCTION

Cation exchange is a feature of many biological systems, both plant and animal, and that associated with plant roots has been actively studied during the past decade. Most workers, following soil cation-exchange capacity (C.E.C.) procedures have expressed their results as milligram-equivalents (me) per 100 g dry roots. A valid objection to this would be that since root exchange is largely a surface phenomenon, the results would best be expressed as me per unit of surface area. Unfortunately it has not proved practicable to estimate the surface area of roots except in the case of certain citrus roots which could be regarded as cylinders of determinable length and cross section [12].

This difficulty could be overcome by the use of disks of storage tissue, whose surface area could be accurately measured. Although a detailed study of their exchange properties has not been made, such disks have been widely used in experiments on salt absorption, since they provide a ready source of physiologically uniform material. This is obviously true when parenchymatous tissues such as potato and swede are used as the source of material but it can also be said of tissue from anatomically complex roots such as carrot and beet provided that a sufficiently large sample of disks is used. Previous studies on such disks have shown that results are highly reproducible [10].

For the purpose of this study, which was complementary to a more extensive investigation of the metabolism of disks of storage tissue [8 11], the disks were maintained under the conditions normally

used in this laboratory. This treatment induces in the disks protoplasmic changes leading up to synthetic activity and culminating in cell division. Cellular activity of this type would almost certainly be accompanied by changes in the pectin content of the disks and since it has recently been shown that 70 to 90 per cent of the C.E.C. of plant roots is directly attributable to free carboxyl groups of pectin [7] it was thought that disks would be suitable material in which to examine the relationship between C.E.C. and pectin.

Differences in the C.E.C. of different plants, coupled with the application of Donnan equilibria principles to the systems have been used to explain to some extent the differential sorption of K and Ca by monocots and dicots [2 3 6]. It was considered that cationic changes in the disks (caused by ion absorption from the tap water in which they were stored[11]) might be explicable in terms of the effects of exchange-capacity changes on the relative proportions of divalent and monovalent cations sorbed by the disks (the valence effect).

The object of the present study was therefore to measure the changes in C.E.C. of disks of storage tissue with time and to attempt tolerate these to concurrent changes in their pectin content.

EXPERIMENTAL

The procedure for preparing the disks was as follows. Washed storage organs of sugar beet, red beet, potato, carrot, and swede turnip were sliced on a ham slicer. The slices were either 0.5 or 1 mm thick, and several slices were fitted together and disks struck from them using a sharp cork-borer of 11 mm diameter. Initially the choice of disk thickness was determined purely by considerations of the hardness of the tissue, and its storage behaviour in the disk washer. For example, 0.5-mm potato disks were never used because they disintegrated after a few days. Even at 1-mm thickness, the disks only lasted for about 7 days at 25°C. After cutting, the disks were washed thoroughly in tap water, and were then transferred to the storage apparatus in which they were maintained at constant temperature (2° or 25°C) in aerated, running tap water [9].

The cation-exchange capacities of the disks were determined, using an acid-washing technique [1], at daily intervals during the storage period. Briefly, the disks (usually 20) were agitated in a basket of plastic gauze in ice-cold 0.01*N* HCl for 2 periods each of 5 minutes, washed free from acid, placed in 200 ml *M* KCl, and titrated to pH 7 with 0.01*N* KOH over a 5-minute period. After washing free from KCl, the disks were dried overnight at 80°C. The results were either expressed as me per 100 g dry matter or as μe per g of initial fresh weight, (*i.e.* fresh weight on day 0) which, in the case of 1-mm disks, corresponded to 10 disks. As shown by the duplicate determinations in Table 2, the reproducibility is satisfactory.

Due to the small size of daily samples, a micromethod for uronic acids [13] was used in which the CO_2 evolved from the dried disks after heating at 111°C with 12 per cent (w/w) HCl in a sealed ampoule for 5 hours, was estimated in the Van Slyke apparatus. The results have been expressed as μg pectin per g initial fresh weight, by assuming all the CO_2 came from galacturonic acid and dividing the weight of CO_2 (in mg) by 44.

This method of estimation includes methyl pectin and non-pectic substances yielding CO_2 which are not considered to take part in cation-exchange processes. In correlating C.E.C. and pectin content Keller and Deuel [7] corrected their pectin values by subtracting an amount equivalent to this methyl pectin fraction, which was estimated by measuring the increase in C.E.C. following demethylation of the roots. Their method was used here and demethylation was achieved by placing a known number of disks in contact with a 0.1*N* NaOH – *M* NaCl solution for 2 hours with occasional mixing. After washing free of the saponifying solution the C.E.C. of the disks was measured in the usual way.

RESULTS AND DISCUSSION

In order to give some idea of how the exchange capacity of these storage tissues compares with that of plant roots, some results (on day 0) have been expressed on a dry-weight basis and are presented in Table 1 along with values for various plant roots taken from the literature. The exchange capacities of plant roots of monocots and dicots fall broadly into two groups, the latter being approximately twice the former, averaged over the common agricultural crops. Larkspur is included here since it appears to have the highest C.E.C. so far recorded.

The values found for the storage tissues are comparable with those reported for plant roots, but there appears to be no connection between the C.E.C. of roots and that of disks taken from storage

TABLE 1

Cation-exchange capacities of tissue disks and plant roots
(as me per 100 g dry weight)

Tissue disks		Roots		Reference
Potato	11.8 (18.0) *	Wheat	9.0	(2)
Red beet	15.8 (32.0)	Oats	22.8	(2)
Swede turnip	25.6 (73.5)	Potato	38.1	(2)
Carrot	34.8 (43.0)	Red beet	51.3	(3)
Sugar beet	50.8 (65.7)	Carrot	51.7	(3)
		Larkspur	94.4	(4)

* Values in parentheses are the maxima reached by the disks during the 10-day storage period at 25°C.

tissue of the same plant. The maximum values reached during storage represent substantial increases on those of day 0, especially in the case of turnip, red beet and potato. These large increases in C.E.C. arise from a decrease in the dry weight of the disks [8] rather than from any increase in the titration value. Certain tissues lose weight more rapidly than others, and the effect of acid-washing and immersion in *M* KCl during titration may also cause slight weight losses.

Effect of various treatments on C.E.C.

1. Effect of killing. Measurements of the exchange capacity of dead roots reported in the literature have shown that they have about the same C.E.C. as living roots. Results in this laboratory indicate that killing by ether (2-hour immersion) or by boiling in water for 5 minutes produces slight increases in root C.E.C. This is not entirely unexpected: firstly, the rupture of the cell walls will expose fresh sites, and secondly, the loss of cell contents will result in a higher C.E.C. if the results are expressed on a dry-weight basis. Similar effects were produced in killed disks and Table 2

TABLE 2

Effect of boiling in water or ether-killing on C.E.C. of sugar-beet, red-beet, and potato disks (μe per g initial fresh weight)

Day	Tissue	Treatment of disks		
		Fresh	Boiled *	Ether-killed
0	Sugar beet	31	33	—
		31		
	Red beet	23	25	—
		25		
	Potato	11	11	—
		12		
1	Sugar beet	32	—	34
		31		37
	Red beet	24	—	28
		24		27
	Potato	11	—	15
		13		14

* Single determinations. Sugar-beet and red-beet disks were 0.5 mm thick; potato 1 mm thick. Stored at 25°C.

shows changes in C.E.C. produced in disks by ether or by boiling in water for 5 minutes (20 disks in 40 ml water). Since the results are expressed on a fresh-weight basis, the differences may represent an increase in the number of available exchange sites brought about by treatment.

Further treatment effects on C.E.C. of red-beet disks are shown in Table 4, which will be discussed in a later section dealing with the C.E.C.-pectin relationship. However, it is clear from the table that boiling disks in water for 5 minutes, or refluxing in alcohol, or refluxing followed by boiling in water, all cause a similar, slight increase in C.E.C. The advantages of boiling the disks appear to be twofold (a) the disks are killed and so metabolic processes are arrested and (b) easily soluble pectic substances, not concerned in cation-exchange processes, are removed from the disks.

2. Effect of time. Preliminary experiments with sugar beet, red beet, and potato gave very small changes in C.E.C. (as μe per g initial fresh weight) over a period of 12 days. This was also found in a later experiment where disks of all five tissues (1 mm thick except sugar beet which were 0.5 mm thick) were stored at 25°C for 10 days. The data for disks (boiled in water for 5 minutes) are shown in Table 3 from which it will be seen that the C.E.C. of each material reaches a maximum 3 to 4 days after cutting. The effect

TABLE 3

Percentage changes in C.E.C. of boiled disks * with time (stored at 25°C)

Tissue	Disk thickness (mm)	Days stored								
		0	1	2	3	4	7	8	9	10
Sugar beet . .	0.5	100	87	83	107	102	92	100	102	97
Red beet . . .	1.0	100	96	104	133	125	104	—	116	—
Potato	1.0	100	94	111	111	111	83	—	—	—
Carrot	1.0	100	107	121	114	128	121	118	110	107
Swede turnip .	1.0	100	111	108	123	127	104	96	88	84

* 20 disks boiled in 40 ml water for 5 minutes.

of disk thickness on the C.E.C. value was eliminated by expressing the results as a percentage of the C.E.C. on day 0, which enables valid comparisons to be made between the five tissues. These percentage increases were small when compared with the magnitude of other changes in the tissues *e.g.* respiration [10]. However, the

C.E.C. and peak of metabolic activity both reached their maximum at about the same time.

When the changes in mineral composition of the disks with time [11] were examined, it was found that selective absorption, particularly of Na by the beet tissues, caused a steady decrease in the ratio of divalent to monovalent cations absorbed. The changes in C.E.C. were very small in themselves, so that it is hardly surprising that the valence effect is not seen in the face of so much active ion absorption and accumulation by the disks. While it seems possible to demonstrate the valence effect in short-term experiments with excised roots in clay suspensions [5], it appears to be less easy to do so from the analysis of mature plant roots due to translocation processes [1].

TABLE 4

C.E.C. and pectin content (both as μe per g initial fresh weight) of 1-mm thick red-beet disks

Treatment	C.E.C.	Pectin content
Fresh disks, untreated	18	81
Boiled 5 minutes in water	21	58
Refluxed in EtOH for 30 minutes	24	69
then boiled in water 5 minutes	22	55
,, ,, ,, ,, 30 ,,	20	45
,, ,, ,, ,, 1 hour	18	44
,, ,, ,, ,, 6 ,,	19	30
,, ,, ,, ,, 12 ,,	18	19

3. Effect of disk thickness and duration of acid wash. During the investigation, it became clear that C.E.C. was not strictly proportional to either the surface area or the volume of the disks.

Although cation exchange is a rapid reaction, earlier work with roots had shown that an appreciable time of acid wash was required if the values obtained were to be comparable with data obtained by electrodialysis. Graphs for roots of various plant species were produced in which C.E.C. was plotted against duration of acid wash [1]. In all cases the curve reached a maximum, flattened off and became parallel to the time axis after some period, invariably less than 10 minutes. The roots used in these studies had diameters varying between 0.5 and 1.0 mm.

It seemed desirable at this stage to attempt to distinguish between surface exchanges and exchanges occurring within the disk. Red-beet disks of 0.5, 1, 2 and 4 mm thickness were given acid washes of 30 sec, 1, 5, 10, 25, and 60 minutes. The total surface area was kept as constant as possible by using 20, 19, 16, and 13 disks which gave total surface areas of 42.0, 42.8, 41.6, and 42.6 sq. cm respectively.

In Table 5 the titration values are given as ml KOH per 10 disks and the ratios calculated by taking the titre for 0.5-mm disks at each washing time as 1.00. For each length of acid wash it will be seen that the titration values per disk have to increase as 1 : 1.07 : 1.24 : 1.56 if surface sites only are involved in the exchange process, while if the entire tissue volume is involved the ratio would be 1 : 2 : 4 : 8.

Only with a 30-second acid wash are ratios of titres obtained for the different thicknesses which agree with the ratios of surface area. Even with a 1-minute wash the titres have increased beyond that required for purely surface exchange sites and this divergence becomes greater as the length of acid wash is increased. This is particularly evident with the thicker disks where, for instance, at 60 minutes the 4-mm disks require nearly twice the expected volume of alkali. On the other hand the titres never approach the high increments with increasing disk thickness which would indicate exchange on a volume basis.

If the data are examined graphically, by plotting (for each disk thickness) the titre per 10 disks against time of acid wash, curves similar to those obtained in the root studies are produced. The smoothness of the 0.5-mm curve seems to imply that all available sites (both external and internal) have been satisfied by washes longer than 5 minutes. While this may be true for the 0.5-mm disks, the fact that titrations do not increase by a factor of two for a doubling in disk thickness must indicate that exchange on a volume basis does not occur in the case of 1-mm disks.

Even with the 0.5-mm or thinner disks this approach cannot conclusively prove that the whole volume is involved in the exchange measurements. Some independent estimation of the total number of exchange sites is required by a chemical method. If it can be assumed that pectic substances are related to the C.E.C., confirmation of the above results would be provided by the pectin analysis, as carried out here, since it is measured on a volume basis.

Preliminary studies on the C.E.C. and pectin content of disks

As illustrated by the values for red-beet disks in Table 4, the pectin content of fresh disks was found to be much greater than the C.E.C. Various types of pretreatment of the disks to reduce this discrepancy suggested themselves and Table 4 sets out the results of these tests. Boiling plant material in 80 per cent alcohol is a standard procedure for removing non-polymeric substances and cell contents. When used here, it gave a larger increase in C.E.C. than did boiling the disks in water, but the reduction in "pectin" content was not so large.

An increase in the length of boiling in water, following alcohol treatment, caused a narrowing in the pectin/C.E.C. values until, after 12 hours they were of the same order, due to the pectin having fallen by 75 per cent. This continued boiling appears to remove substances yielding CO_2 on decarboxylation but not contributing to the C.E.C., since the exchange capacity changes only slightly. A fuller account of these changes will appear elsewhere [8]. Similar results were obtained with sugar-beet disks boiled in water for increasing periods but without the initial boiling in alcohol.

The decarboxylation method includes CO_2 derived from methylated groups of pectin which do not take part in cation exchange. In order to determine the degree of esterification and make a correction for it in the pectin values Keller and Deuel [7] adopted a saponification technique. The difference in exchange capacity between saponified and unsaponified tissues gave a measure of the methylated pectin. From these values and the pectin content they were able to calculate the percentage contribution (X) of free carboxyl groups of pectin to the C.E.C. by the formula: –

$$X = \frac{P_t - (T_v - T_o)}{T_o} \times 100$$

where P_t = pectin content (by decarboxylation)
T_v = C.E.C. of saponified material
T_o = C.E.C. of unsaponified material.

This formula was tested with fresh disks of the five tissues (all 0.5 mm thick except potato which were 1 mm thick) and gave values for X much greater than 100 in the case of first three tissues and slightly less than 100 for carrot and turnip (Table 6). This confirmed the earlier results with red beet disks.

TABLE 5

Red-beet disks: divergence of titres from those predicted (calculated) if only surface exchange sites are concerned in exchange process (titres are ml 0.01*N* KOH per 10 disks)

Time of acid wash		30 sec		1 min		5 min		10 min		25 min		60 min	
Disk thickness (mm)	Ratio of surface areas	Titre (ml)	Calc. ratio	Titre (ml)	Calc. ratio	Titre (ml)	Calc. ratio	Titre (ml)	Calc. ratio	Titre (ml)	Calc. ratio	Titre (ml)	Calc. ratio
0.5	1.00	0.e-	1.00	1.00	1.00	1.27	1.00	1.20	1.00	1.27	1.00	1.15	1.00
1.0	1.07	0.93	1.06	1.32	1.32	1.38	1.09	1.59	1.33	1.62	1.28	1.73	1.50
2.0	1.24	1.01	1.15	1.41	1.41	1.46	1.15	1.56	1.30	1.52	1.20	2.18	1.80
4.0	1.56	1.38	1.57	2.17	2.17	2.10	1.65	2.18	1.82	2.28	1.80	3.15	2.74

TABLE 6

The percentage contribution (X) of the free carboxyl groups of pectin towards the cation exchange capacity of tissue disks

Tissue	Thickness (mm)	Fresh				Boiled			
		Pectin P_t	C.E.C. * Unsap. T_o	C.E.C. * Sap. T_v	X	Pectin P_t	C.F.C. * Unsap. T_o	C.F.C. * Sap. T_v	X
Sugar beet	0.5	91	43	65	160	52	37	55	92
Red beet	0.5	90	36	59	190	52	36	51	100
Potato	1.0	33	16	17	198	24	20	16	140
Carrot	0.5	59	46	67	83	47	48	66	60
Swede turnip	0.5	64	48	67	95	48	46	63	68

* As μe per g initial fresh weight. Determined on Day 9. Stored at 2°C.

When the same procedure was applied to disks which had been first boiled in water for 5 minutes, the values of X (with the exception of potato) were less than 100, ranging from 90 to 100 for beet to 60 to 70 for carrot and turnip (Table 6). These values agree with the values obtained by Keller and Deuel[7] with root material where the contribution of pectin towards the exchange capacity was always of the order of 70 to 90 per cent.

The relationship between C.E.C. and pectin content of sugar-beet disks

Consequent on the results obtained in the disk-thickness experiment and the preliminary studies of the pectin–C.E.C. relationship, it was decided to test Keller and Deuel's hypothesis more rigorously by following the pectin and C.E.C. changes in 0.5-mm sugar-beet disks stored at 25°C over a 10-day experimental period. Daily determinations of pectin and the C.E.C. of unsaponified and saponified boiled disks were made and the results are given in Table 7.

TABLE 7

The percentage contribution (X) of free carboxyl groups of pectin towards the cation-exchange capacity of 0.5 mm thick sugar beet disks

Day	Pectin content P_t	C.E.C. Sap. T_v	C.E.C. Unsap. T_o	Corrected pectin value $P_t - (T_v - T_o)$	X (%)
0	63	51	41	53	129
1	53	44	37	46	124
2	45	46	34	33	97
3	50	52	44	43	98
4	58	56	42	44	105
7	51	53	39	36	92
8	48	48	41	42	102
9	46	45	43	43	100
10	45	45	40	39	98
					Mean 105

All as μe per g initial fresh weight. Stored at 25°C.

When the results are expressed graphically (Fig. 1) the quantitative agreement between pectin and C.E.C. is extremely good and their respective curves reach their maximum on the same day.

It is not clear why pectin is rather higher than C.E.C. on days 0 and 1, and then correlates with it for the remainder of the experimental period. It can be seen, however, that similar trends were

shown (Fig. 2) by potato disks (1 mm thick stored at 25°C), the values of X on days 0 and 1 being 130 and 139 per cent. It will be recalled that potato was too soft a tissue for storage in the disk washer at thicknesses less than 1 mm. However one result of this high permeability was that it was possible to obtain C.E.C. measure-

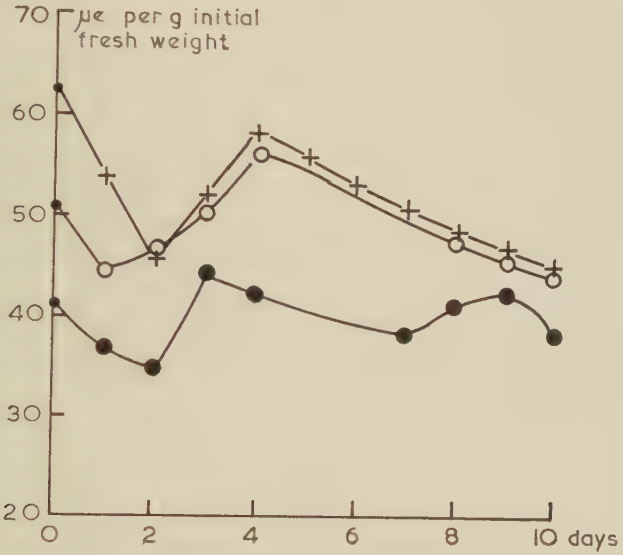

Fig. 1. Changes in pectin content (+), C.E.C. of unsaponified (●), and saponified (○) sugar-beet disks with time.

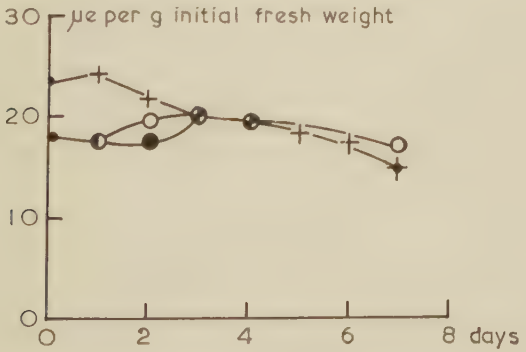

Fig. 2. Changes in pectin content (+), C.E.C. of unsaponified (●), and saponified (○) potato disks with time.
Concurrent points are indicated by ◐ and ◒.

ments on a volume basis on this particular tissue for disks 1 mm thick.

According to the present findings, the free carboxyl groups of pectin alone appear to account for the entire exchange capacity of beet and potato disks. It should be borne in mind, however, that our analytical procedure measures total CO_2 derived from decarboxylation, which it has been assumed comes from pectic substances only. The validity of this assumption for plant roots has been discussed at some length by Keller and Deuel [7].

It is felt that the present experiment provides a very stringent test of Keller and Deuel's hypothesis since the correlation was obtained over a 10-day period in contrast to their figures which were obtained at one point in time in a plant-growth cycle.

All in all, taking the Swiss results with plant roots, and the present results, with tissue disks, the good measure of agreement between C.E.C. and pectin content, reached by contrasting methods, suggests that the ability of cell material to exchange cations and its pectin content are linked.

SUMMARY

The cation-exchange capacity (C.E.C.) of disks of storage tissue of sugar beet, red beet, potato, carrot, and swede turnip kept in running tap water at constant temperature, has been measured using an acid-washing technique. The pectin content of the disks has been estimated by measuring the CO_2 evolved on decarboxylation.

There is quantitative agreement between exchange capacity and pectin content of the disks provided the former is measured on a tissue volume basis, and also provided that in assessing the latter, the substances yielding CO_2 yet not participating in cation exchange are first removed from the tissues by boiling in water. The C.E.C. and pectin content of the disks increase with time and reach a maximum 3 to 4 days after the disks are cut from the parent tissue.

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DOSAGE DU FER ET DE L'ALUMINIUM ÉCHANGEABLE DANS LES MINÉRAUX ARGILEUX ET DANS LES SOLS *

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INTRODUCTION

De nombreuses études ont été effectuées sur l'utilisation de l'oxine et de ses dérivés comme réactif spécifique pour le dosage colorimétrique de certains éléments minéraux [8 9 12]. Il semble que l'influence des divers facteurs déterminant la précision du dosage et leurs interactions n'aient pas encore été complètement éclaircie, il en résulte dans la littérature une certaine confusion et des contradictions apparentes en ce qui concerne les conditions d'extraction des oxinates en fonction du pH et du nombre d'extractions [1 7 8 10]. Divers auteurs ont également étudié l'influence de la nature du solvant et du nombre d'extractions [11 13].

Cette note a pour but de préciser l'influence de la concentration en oxine sur le nombre d'extraction et sur la zone de pH où l'extraction des oxinates de fer et d'aluminium est quantitative et spécifique. Nous présenterons pour terminer une méthode rapide pour le dosage de ces éléments présents dans une même solution. Cette méthode a été mise au point pour le dosage du fer et de l'aluminium présents à l'état échangeable dans les minéraux du sol et désorbés par du $BaCl_2$ ou du NaCl.

Récemment Umland et Hoffman [14] et avant eux Alten et ses collaborateurs [2 3] ont attiré l'attention sur la possibilité de solubiliser l'oxinate de magnesium en présence de butylamine ou

* Publication du Centre de Chimie Biologique et Colloïdale du sol subsidié par l'I.R.S.I.A.

d'acide sulfanilique, les essais que nous avons effectués afin d'adopter ce dosage aux conditions qui nous concernent n'ont pas donné satisfaction.

Le principe de la méthode par extraction [8] est basé sur la différence de solubilité des oxinates métalliques dans le solvant et dans l'eau. Le coefficient de partage est déterminé par le rapport des produits de solubilité : le nombre d'extractions requis sera d'autant plus faible que le coefficient de partage sera plus élevé.

Le coefficient de partage dépend en outre du rapport des volumes en présence, de la concentration de la solution aqueuse en aluminium et en fer et de la concentration en oxine de la solution chloroformique. Lacroix [8] a fait une étude mathématique de ces équilibres.

MODE OPÉRATOIRE

Nous avons toujours utilisé une ampoule à décantation de 100 ml, un volume de solution aqueuse de 25 ml contenant moins de 25 γ d'aluminium ou de fer, un volume de 5 ml de la solution chloroformique d'oxine. On recueille par décantation les fractions successives de la solution chloroformique d'oxinate dans un ballon jaugé de 50 ml que l'on porte au volume avec du chloroforme.

Pour la colorimétrie, nous utilisons le Spectrophotometer Beckman, modèle B. Les maxima d'absorption des solutions d'oxinate ont été déterminés par Moeller [9] soit 370 mμ pour le fer et 395 mμ pour l'aluminium.

RÉSULTATS

Influence de la concentration en oxine sur le nombre d'extractions

La Fig. 1 montre que le nombre d'extractions nécessaires pour obtenir une extraction quantitative diminue quand la concentration en oxine de la solution chloroformique augmente. Ainsi, pour une concentration en oxine 0,01*M* dans le chloroforme il faut au moins huit extractions pour atteindre 100% d'extraction, tandis qu'avec une solution 0,04*M* trois extractions suffisent. La Fig. 2 montre que la concentration en aluminium et en fer de la solution aqueuse influe également sur le nombre d'extractions.

De ces données on peut conclure qu'un dosage quantitatif de l'aluminium peut être exécuté avec une concentration en oxine 0,03*M* et quatre extractions pour autant que la concentration en aluminium ne dépasse pas 1 γ de ml de solution aqueuse, les rapports

des volumes solution – solvant étant ceux qui sont indiqués. La dernière extraction sera presque toujours incolore.

Des figures analogues peuvent être obtenues pour le fer; elles

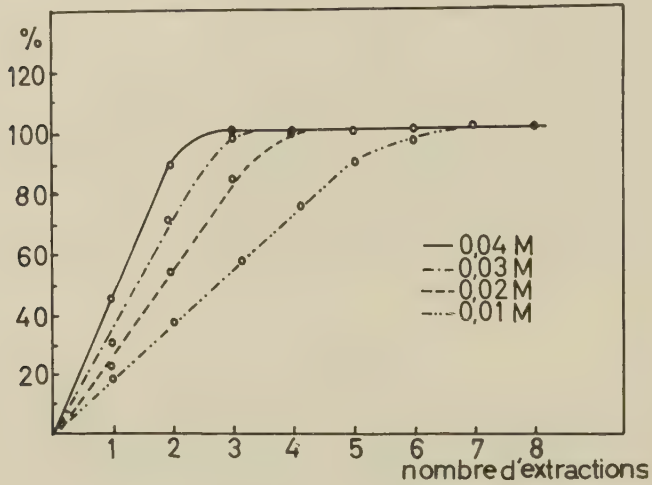

Fig. 1. Nombre d'extractions nécessaire pour obtenir 100% d'extraction de l'aluminium présent en fonction de la concentration en oxine dans le chloroforme. Quantité d'aluminium 20μe pour une prise d'essai de 25 ml.

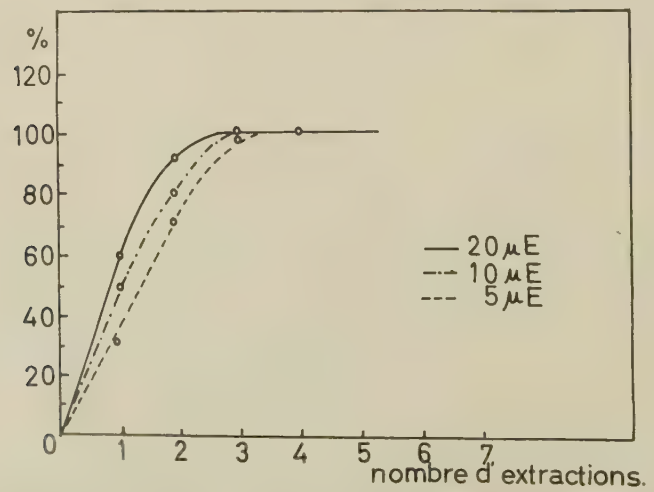

Fig. 2. Nombre d'extractions nécessaire pour obtenir 100% d'extraction en fonction de la concentration en aluminium de la solution aqueuse. Concentration en oxine 0,03*M* dans le chloroforme.

montrent que deux extractions avec cinq ml de chloroforme 0,03*M* en oxine permettent d'obtenir une extraction quantitative de cet élément.

Influence de la concentration en oxine et du pH sur le pourcentage d'extraction des oxinates de fer et d'aluminium

Des solutions d'aluminium contenant 80 µe, 100 ml sont portées à différents pH. L'extraction est faite sur 25 ml de ces solutions avec quatre fois cinq ml de chloroforme 0,03*M* et 0,01*M* en oxine. De même pour des solutions de fer. L'extraction se fait avec deux fois cinq ml de chloroforme 0,03*M* en oxine.

La quantité d'aluminium et de fer extrait à chaque pH est calculée en $^{o}_{o}$ de la quantité totale présente. Les résultats sont présentés à la Figure 3.

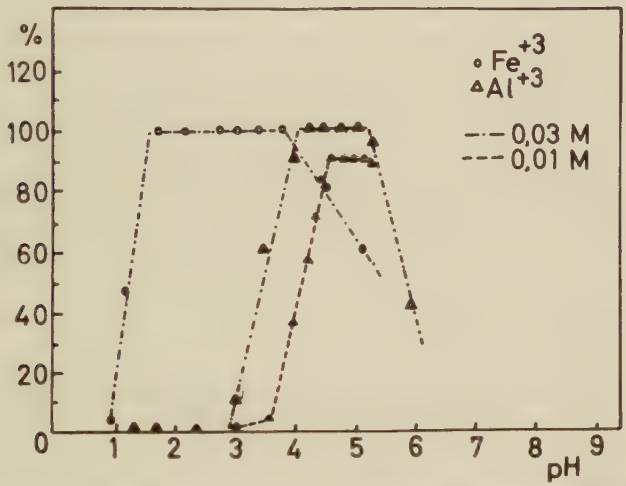

Fig. 3. Variation de la quantité d'élément extrait en fonction du pH pour les conditions d'expériences citées.

La Figure 3 montre que la concentration en oxine de la solution chloroformique a une importance considérable sur l'étendue de la zone de pH où l'extraction est quantitative. On remarquera qu'on ne peut atteindre une extraction totale de l'aluminium après quatre extractions avec une solution de chloroforme 0,01*M* en oxine.

Cette expérience permet de rejoindre celle de Moeller [10] d'une part, celle de Lacroix [8], Gentry et Sherrington [6] d'autre part. Le premier trouve une très grande sélectivité en pH 4,3 et 4,6 où

l'extraction de l'aluminium est quantitative; il utilise de faibles concentrations en oxine (0.01M) et plusieurs extractions. Les seconds extraient la totalité de l'aluminium en une seule opération et la zone de pH s'étend de 3 à 11,5, ils utilisent des concentrations en oxine relativement élevées de l'ordre de 0,1M. On voit donc que les techniques décrites dans la littérature sont soit quantitatives et manquent de sélectivité, soit sélectives mais nécessitent alors un nombre exagéré d'extractions.

Le dosage successif du fer et de l'aluminium tel que le rapporte Alexander [1] est aisé étant donné que le fer est totalement extrait entre pH 1,7 et 3,8 et qu'il ne peut plus gêner le dosage de l'aluminium. Cette méthode est plus rapide que la complexation du fer par le ferrocyanure [1], ou d'autres méthodes [6]; elle permet en outre le dosage successif et rapide de ces deux éléments.

On peut conclure que les limites d'extraction quantitative des oxinates de fer et d'aluminium par le chloroforme sont fonction de la concentration en oxine de la solution de chloroforme, du nombre d'extractions, du rapport des volumes de la solution aqueuse et de la solution chloroformique. Ces limites de pH sont pour l'oxinate de fer comprises entre pH 1,7 et 3,8 et pour l'oxinate d'aluminium entre pH 4,25 et 5,0, dans les conditions d'expériences citées.

MÉTHODES D'ANALYSE

Dosage du fer et de l'aluminium

Solution de réactifs: Oxine dans le chloroforme 0,03M
Acetate de sodium 0,1M
Chloroforme.

Les solutions à analyser sont portées à pH = 2.

Dans une ampoule à décanter de 100 ml pipetter 25 ml de la solution inconnue contenant moins de 25 µe de fer ou/et d'aluminium.

Dosage du fer. Ajouter dans l'ampoule à décanter 5 ml de la solution d'oxine chloroformique 0,03M. Agiter en évitant la formation de mousse. Laisser reposer quelques instants pour obtenir des solutions limpides. Le chloroforme se colore en vert-noir. L'oxinate de fer dissout dans le chloroforme est décanté dans un ballon jaugé de 50 ml. Cette extraction est répétée trois fois. Le ballon jaugé est alors porté au volume avec du chloroforme pur. Colorimétrer à 470 mµ en mesurant la transparence par rapport au chloroforme pur (l'oxine n'absorbe pas à cette longueur d'onde).

Dosage de l'aluminium. Ajouter dans l'ampoule à décanter environ 10 ml de la solution d'acétate de sodium 0,1M. L'oxinate d'aluminium

insoluble dans l'eau à ce pH précipite en jaune-vert. Extraire quatre fois avec 5 ml de la solution d'oxine chloroformique 0,03*M*. Récolter les fractions successives dans un ballon jaugé de 50 ml. Porter au volume avec du chloroforme pur et colorimétrer à 395 mμ par rapport au chloroforme.

Précision de la méthode

Tant l'oxinate de fer que l'oxinate d'aluminium obéissent parfaitement à la loi de Lambert-Beer dans la gamme des concentrations utilisées et aux longueurs d'onde citées quand on utilise un B Spectrophotometer Beckman.

Nous avons vérifié que les ions suivants ne gênent pas: Cl^-, NO_3^-, SO_4^{--}, Ba^{++}, Na^+, K^+, Ca^{++}, Mg^{++}.

Nous avons controlé la précision de la méthode en déterminant le pourcentage de recouvrement de quantités connues d'aluminium et de fer ajoutées à une solution d'extraction au $BaCl_2$ normal.

Les quantités présentes variaient de 0.1 à 0.7 me/l. La colorimétrie de ces solutions nous permet de retrouver 101,3 ± 1,5% du fer et 101,2 ± 2.0% de l'aluminium ajouté.

Récupération du chloroforme

Le chloroforme utilisé pour le dosage peut facilement être récupéré. Le chloroforme est lavé par deux fois avec 50 ml d'HCl concentré dans une ampoule à décanter. Ensuite, il est lavé à l'eau distillée jusqu'à neutralité des eaux de lavages controlée au papier tournesol.

Le chloroforme est alors distillé et après distillation séché par passage sur du Na_2SO_4 ou CaO. Il peut alors être réutilisé pour le dosage colorimétrique du fer et de l'aluminium.

RÉSUMÉ

Une méthode est proposée pour le dosage du fer et de l'aluminium échangeable dans les minéraux argileux et dans les sols. La méthode est basée sur l'extraction successive des oxinates de fer et d'aluminium en fonction du pH.

Les conditions optimales et l'influence des divers facteurs déterminant l'extraction quantitative et sélective de ces deux éléments ont été préalablement étudiées.

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DIE ANIONENAUSTAUSCHERSUBSTANZEN ALUMINIUM- UND EISEN (3)-HYDROXYD-SILIKAT-PHOSPHAT-HUMAT ALS MINERALE DES BODENS

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Die bekannte Erscheinung, daß Kationen und Anionen von Böden adsorbiert werden, und gleichzeitig andere Kationen und Anionen in Lösung gehen, kann zwei Ursachen haben: Erstens können doppelte Umsetzungen zwischen stöchiometrisch definierten Substanzen mit definierten Löslichkeitsgleichgewichten stattfinden. Diese Substanzen sind u.a. dadurch gekennzeichnet, daß sie im Gleichgewicht mit Lösungen innerhalb eines *Bereiches* der Konzentrationen der in ihnen vorkommenden Ionen eine konstante Zusammensetzung aufweisen. Zweitens kann der Ionenaustausch durch Ionenaustauscher erfolgen. Diese Substanzen (siehe z.B. die ausführliche Darstellung der Gesetzmäßigkeiten des Ionenaustausches von Grießbach [16], S. 80–201) stellen polyvalente Festionen dar, an die austauschbare Ionen adsorbiert sind. Nach neueren Erkenntnissen sind sie als feste, konzentrierte Elektrolyte anzusehen, weil im Gleichgewicht die Aktivitäten der an den Ionenaustauschern befindlichen Ionen in weitem Bereich eine Funktion der Aktivitäten der gelösten Ionen sind **:

$$\left(\frac{a_B}{a_A}\right)_f = K_a \left(\frac{a_B}{a_A}\right)_l. \qquad (1)$$

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** Dieser Auffassung der Ionenaustauscher als feste Elektrolyte stehen, wie Grießbach [16] eingehend darlegte, die zahlreichen älteren Formulierungen von Austauschgleichgewichten gegenüber, deren Aufstellung nach mehr oder weniger gut bestätigten Gesetzen, z.B. dem Massenwirkungsgesetz und der Freundlich-Langmuirschen Adsorptionsisotherme oder auf Grund empirischer Beziehungen (Ganssen, Wiegner und Jenny, Vageler u.a.) erfolgte.

In dieser Gleichung bedeuten (a_A und $a_B)_f$ die Aktivitäten von Kationen oder Anionen am festen Ionenaustauscher, (a_A und $a_B)_l$ die Aktivitäten in der Lösung, K_a die wahre Massenwirkungskonstante, die den Aktivitäten aller beteiligter Ionen in der festen Phase und in der Lösung Rechnung trägt.

Daher besitzen die Austauschersubstanzen keine stöchiometrisch definierte Zusammensetzung.

Führt man in Gl. (1) statt der Aktivitäten analytisch erfaßbare Größen ein, d.h. für die feste Phase die Molenbrüche * X_A und X_B und für die Lösungsphase die analytisch gemessenen Konzentrationen ** C_A und C_B, so ergibt sich:

$$\frac{X_B}{X_A} = \frac{C_B}{C_A} \cdot D_A^B. \qquad (2)$$

D_A^B = Selektivitätskoeffizient.

Eine Unterscheidung, ob eine doppelte Umsetzung an stöchiometrisch definierten Substanzen oder eine Reaktion an Ionenaustauschern erfolgt, kann nicht durch Behandeln einer Substanz oder eines Bodens mit Lösungen und Bestimmen der gebundenen und in Lösung gegangenen Ionen getroffen werden, weil sowohl doppelte Umsetzungen an stöchiometrisch definierten Substanzen als auch Reaktionen an Ionenaustauschern nach der gleichen Gesetzmäßigkeit, dem Massenwirkungsgesetz verlaufen. Vielmehr muß entweder die Entstehung von stöchiometrisch definierten Substanzen (Kennzeichen: konstante Zusammensetzung innerhalb eines Konzentrationsbereiches) oder das Vorkommen von Austauschern (Kennzeichen: Abhängigkeit der Molarprozente der austauschbaren Ionen von ihren Konzentrationen in weitem Bereich nach Gl. (1) und (2) aufgezeigt werden †).

Es besteht allerdings die Möglichkeit, daß stöchiometrisch definierte

* Der Molenbruch ist die Molzahl (Gewicht/Molekulargewicht) eines Bestandteiles in einer Substanz, dividiert durch die Gesamtmolzahl in dieser Substanz. Die Summe der Molenbrüche in einer Substanz beträgt 1. Setzt man sie gleich 100, so erhält man die Molarprozente. Dieser letztere Ausdruck wird im Folgenden verwendet.

** In stark verdünnten Lösungen (unter $N/10$) sind die Aktivitäten den Konzentrationen gleich zusetzen.

† Ohne Anwendung von Gleichung (1) und (2) wurde der Nachweis, daß eine Austauschreaktion an kristallinen Austauschern (Tonmineralien) von bekannter Korngröße und Oberfläche erfolgt, von Hofmann und Mitarbeitern [41] dadurch geführt, daß die Reversibilität des Austausches, das Austauschvermögen und auch der Ort der austauschenden Ionen (Kristallecken, -kanten) festgestellt, und eine doppelte Umsetzung durch Bildung einer neuen löslichen Substanz erkannt und ausgeschlossen wurde.

Substanzen innerhalb von *kleineren* Konzentrationsbereichen existenzfähig sind, und es experimentell nicht gelingt, eine konstante Zusammensetzung in den Niederschlägen innerhalb dieser kleinen Konzentrationsbereiche festzustellen. Diese Möglichkeit muß z.B. durch Röntgendiagramme untersucht werden (s.u.) und ist um so unwahrscheinlicher, je weiter der Konzentrationsbereich ist, innerhalb dessen die Zusammensetzung der Niederschläge mit den Ionenkonzentrationen im Gleichgewicht kontinuierlich sich ändert.

Die experimentellen Untersuchungen für diese Unterscheidung gestalten sich gewöhnlich sehr schwierig, weil der Aufwand an analytischer Arbeit zur Kontrolle der Gleichgewichtseinstellungen von *verschiedenen* Seiten her sehr erheblich ist *.

METHODIK

Durch eine besondere Methode gelingt es jedoch, Gleichgewichte bei doppelten Umsetzungen oder bei Reaktionen mit Ionenaustauschern sofort und zuverlässig sich einstellen zu lassen. Diese Methode besteht darin, daß die Substanzen, die darauf geprüft werden sollen, ob sie stöchiometrisch definiert sind oder Austauschersubstanzen darstellen, aus ionendispersen Lösungen ausgefällt werden, und während und nach ihrer Ausfällung verschiedene Konzentrationen der reagierenden Ionen eingestellt und gemessen werden. Mit Hilfe dieser Methode wurden die im Folgenden beschriebenen Gleichgewichtsbestimmungen in den Systemen $Al_2O_3-SiO_2-P_2O_5-$Huminsäure$-H_2O$ und $Fe_2O_3-SiO_2-P_2O_5-$Huminsäure$-H_2O$ ausgeführt.

Aus je einer Bürette wurden in mehreren Ansätzen 50 ccm angesäuerte $M/50$ Aluminium- oder Eisen(3)-chloridlösung und verschiedene Mengen Natriumsilikatlösung ($M/50$ in bezug auf SiO_2) oder $M/50$ Kaliumdihydrogenphosphatlösung oder Natriumhumatlösung (20 g Huminsäure, Merck, gelöst in 1 $N/10$ Natronlauge) in 200 ccm siedendes Wasser tropfen gelassen, dessen pH-Wert durch gleichzeitige Zugabe von Natronlauge mit Hilfe eines zugesetzten Indikators (Bromphenolblau, Bromthymolblau oder Phenolphthalein) verschieden und während der Ausfällung annähernd konstant eingestellt wurde. Nach Beendigung jeder Ausfällung wurde 3 Stunden unter Ersatz des verdampfenden Wassers weiter zum Sieden erhitzt, und aus der siedenden Lösung eine Probe von etwa 10 ccm entnommen, die sofort durch ein trockenes Filter filtriert wurde. Im Filtrat wurde kolorimetrisch die Konzentration an SiO_2 [42], P_2O_5 [23 38] oder Huminsäure ** gemessen. In einer weiteren, aus den siedenden Lösungen entnommenen Probe von etwa 5 ccm wurde nach Abkühlen der pH-Wert mit Hilfe einer Glaselektrode bestimmt.

* Wie Walton [40] angibt, wurden in den meisten Studien über Ionenaustausch, die in der Literatur beschrieben sind, keine echten Gleichgewichte erreicht. Vgl. auch die scharfen, kritischen Bemerkungen von Grießbach [16] sowie von Beaton und Furnas (s. Ref. [16]).

** bei = 436 nm und bei = 578 nm. Die Aufstellung einer Eichkurve erfolgte mit den Verdünnungen der Natriumhumatlösung.

TABELLE 1

Gleichgewichte von Aluminium-, Hydroxyl- und Silikationen enthaltenden Niederschlägen von verschiedenen molaren Mengenverhältnissen Al : Si bei verschiedenem pH-Wert bei 100°

Zugegebene mMol		pH	Gelöste SiO_2 (mMol/200 ccm)	mMol i.d. Niederschl.		Al : Si in den Niederschlägen
Al-Ionen	Silikat-Ionen			Aluminium-ionen	Silikat-ionen	
1,0	0,067	8,0	0,010	1,0	0,057	18 : 1
		6,9	0,006	1,0	0,061	16 : 1
		5,7	0,003	1,0	0,064	16 : 1
		4,2	0,002	1,0	0,065	15 : 1
		3,5	0,025	n.b.		
1,0	0,1	8,0	0,020	1,0	0,080	13 : 1
		7,1	0,015	1,0	0,085	12 : 1
		6,0	0,010	1,0	0,090	11 : 1
		4,5	0,005	1,0	0,095	11 : 1
		3,7	0,020	n.b.		
1,0	0,2	8,0	0,10	1,0	0,10	10 : 1
		6,8	0,060	1,0	0,14	7 : 1
		6,1	0,035	1,0	0,165	6 : 1
		5,0	0,010	1,0	0,19	5,2 : 1
		4,3	0,015	1,0	0,185	5,4 : 1
		3,5	0,035	n.b.		
1,0	1,0	8,0	0,70	1,0	0,3	3,3 : 1
		7,0	0,60	1,0	0,4	2,5 : 1
		5,8	0,50	1,0	0,5	2,0 : 1
		4,7	0,40	1,0	0,6	1,7 : 1
		3,5	0,40	n.b.		

TABELLE 2

Gleichgewichte von Eisen(3)-, Hydroxyl- und Silikationen enthaltenden Niederschlägen von verschiedenen molaren Mengenverhältnissen Fe : Si bei verschiedenem pH-Wert bei 100°

Zugegebene mMol		pH	Gelöste SiO_2 (mMol/200 ccm)	mMol i.d. Niederschl.		Fe : Si in den Niederschlägen
Fe-Ionen	Silikat-Ionen			Eisen-ionen	Silikat-ionen	
1,0	0,067	9,1	0,030	1,0	0,037	27 : 1
		8,2	0,015	1,0	0,052	19 : 1
		6,8	0,015	1,0	0,052	19 : 1
		3,9	0,005	1,0	0,062	16 : 1
		2,8	0,020	n.b.		
1,0	0,1	9,0	0,05	1,0	0,05	20 : 1
		8,4	0,03	1,0	0,07	14 : 1
		6,9	0,02	1,0	0,08	13 : 1
		4,0	0,01	1,0	0,09	11 : 1
		2,9	0,03	n.b.		
1,0	0,2	8,9	0,10	1,0	0,10	10 : 1
		7,7	0,08	1,0	0,12	8,3 : 1
		6,8	0,07	1,0	0,13	7,7 : 1
		4,5	0,04	1,0	0,16	6,2 : 1
		3,6	0,02	1,0	0,18	5,5 : 1
1,0	0,0	9,0	0,8	1,0	0,2	5,0 : 1
		8,1	0,7	1,0	0,3	3,3 : 1
		7,1	0,7	1,0	0,3	3,3 : 1
		5,8	0,6	1,0	0,4	2,5 : 1
		4,7	0,4	1,0	0,6	1,7 : 1
		3,1	0,4	1,0	0,6	1,7 : 1

TABELLE 3

Gleichgewichte * von Aluminium- oder Eisen-, Hydroxyl- und Phosphationen enthaltenden Niederschlägen von verschiedenen molaren Mengenverhältnissen Al : P oder Fe : P bei verschiedenem pH-Wert bei 100°

Aluminiumhydroxydphosphat			Eisenhydroxydphosphat		
Al : P	pH	P_2O_5 mg/l	Fe : P	pH	P_2O_5 mg/l
15 : 1	7,4	1,2	10 : 1	8,0	1,5
	6,5	0,6		6,7	0,7
	5,9	0,3		6,0	0,25
	5,3	0,23		5,2	0,2
	4,3	0,20		4,4	0,12
	3,0	0,27		3,1	0,12
10 : 1	7,6	12	8 : 1	9,0	10,7
	7,0	6		8,1	2,4
	6,3	2,2		6,2	1,4
	4,9	2,0		6,0	0,8
	4,2	2,1		4,9	0,3
	3,2	5,5		3,8	0,2
5 : 1	7,3	22	5 : 1	7,2	3,6
	6,9	15		6,9	3,0
	6,0	11		6,2	2,5
	5,4	7		5,5	2,1
	4,0	7		3,0	1,5
	3,2	11		2,4	2,2

TABELLE 4

Gleichgewichte * von Aluminium- oder Eisen-, Hydroxyl- und Humationen enthaltenden Niederschlägen von verschiedenen molaren Mengenverhältnissen bei verschiedenem pH-Wert bei 100°

Aluminiumhydroxydhumat			Eisenhydroxydhumat		
Al/Hum. **	pH	mg Humat/l	Fe/Hum. **	pH	mg Humat/l
10 : 1	7,5	5,0	10 : 1	7,1	8
	6,3	3,5		6,2	2
	6,0	3,7		5,0	0,3
	5,7	3,2		4,4	0
	4,5	5		3,9	0
	3,9	5,1		3,2	1,2
5 : 1	6,4	4	5 : 1	6,9	12
	5,7	0,5		6,0	2
	4,0	6		4,3	0,2
	3,5	7		3,9	0
				3,2	0,8

* Phosphationen und Humationen wurden bedeutend vollständiger als Silikationen bei den gleichen Mengenverhältnissen ausgefällt, sodaß Al oder Fe : P oder Humat in den Niederschlägen durch die zugesetzten Mengen Ionen angenähert gegeben sind.

** Al/Hum. bezw. Fe/Hum. bedeutet das Verhältnis angewandte ccm *M*/50 Aluminium- bezw. Eisensalzlösung: angewandte ccm Natriumhumatlösung (5 g/l Huminsäure (Merck)).

ERGEBNISSE

Die gemessenen SiO_2-, P_2O_5- und Huminsäurekonzentrationen sind für verschiedene Mengenverhältnisse Al_2O_3 oder Fe_2O_3 : SiO_2 oder P_2O_5 oder Huminsäure in Abhängigkeit vom pH-Wert in den Tabellen 1 bis 4 zusammengestellt *.

Aus den Tabellen ist ersichtlich:

1. Die SiO_2-, P_2O_5- und Huminsäurekonzentrationen in der Lösung sind in *weitem* Bereich um so größer, je höher die Molarprozente an SiO_2, P_2O_5 oder Huminsäure in den Niederschlägen sind. Die ausgefällten Aluminium- bezw. Eisenverbindungen sind also als Austauschersubstanzen für Hydroxyl-, Silikat-, Phosphat- und Humationen anzusehen **.

2. Die SiO_2-, P_2O_5- und Huminsäurekonzentrationen weisen bei verschiedenen pH-Werten Minima auf. Diese Minima entstehen dadurch, daß bei pH-Werten oberhalb der Minima die Molarprozente in den Niederschlägen abhängig von den Konzentrationen in der Lösung sind, und bei pH-Werten unterhalb der Minima eine Auflösung der Niederschläge erfolgt.

Es ließ sich auch in weiteren Versuchen kein kleinerer Bereich der Anionenkonzentrationen auffinden, innerhalb dessen die Abhängigkeit der Konzentrationen in der Lösung von den Molarprozenten in den Niederschlägen sich stärker änderte als außerhalb des Bereiches. Eine Entstehung von stöchiometrisch definierten Verbindungen, z.B. basischen Phosphaten † konnte daher nicht nachgewiesen werden.

Pulveraufnahmen †† der Aluminiumionen enthaltenden Niederschläge zeigten die Linien des Hydrargillits, während die Eisen-

* Bei den pH-Werten oberhalb der Minima der Anionenkonzentrationen sind die zugesetzten Aluminium- und Eisenionen quantitativ ausgefällt. Die zugesetzten Mengen Silikat-, Phosphat- und Humationen sind bis auf die analytisch ermittelten, gelösten Mengen ebenfalls ausgefällt.

** In weitem Konzentrationsbereich konstante Selektivitätskoeffizienten nach Gl. (2) lassen sich jedoch aus den analytisch ermittelten SiO_2-, P_2O_5- und Huminsäurekonzentrationen nicht errechnen, weil diese die Summe der Konzentrationen von neutralen und Acidoionen darstellen.

† Cloutier [7] kommt zu dem Schluß, daß die Existenz stöchiometrisch definierter, basischer Aluminiumphosphate unwahrscheinlich ist, ebenso wie Scheffer und Schulz [33] die Ausfällung stöchiometrisch definierter, basischer Eisenphosphate aus wäßriger Lösung nicht für möglich halten.

†† Frau Dr. Pascal, Mineralogisches Institut der Humboldt-Universität danke ich für die Herstellung und Auswertung der Pulverdiagramme.

ionen enthaltenden Niederschläge sich als röntgenamorph erwiesen, ein Befund, der mit den Untersuchungen von Glemser [15] über die Eigenschaften von frisch gefälltem Aluminium- und Eisenhydroxyd in Übereinstimmung steht. Ein Einfluß des Silikat-, Phosphat- und Humatgehaltes auf das Röntgenspektrum ließ sich nicht erkennen. Auch im Elektronenmikroskop waren keine Strukturen zu bemerken.

Es sei vorgeschlagen, die vereinfachende Bezeichnung Aluminium- und Eisen-Hydroxyd-Silikat-Phosphat-Humat einzuführen. Bei Anwendung dieser Bezeichnung sollte man sich darüber klar sein, daß es sich nicht um eine stöchiometrisch definierte Substanz, sondern um eine Austauschersubstanz handelt.

DISKUSSION

Im Folgenden sollen einige bodenkundliche Literaturstellen besprochen werden, in denen Hinweise für das Vorkommen dieser Austauschersubstanz im Boden enthalten sind, in denen also die Molarprozente der Anionen in Festkörpern in *weitem* Bereich abhängig von den Anionenkonzentrationen in der Lösung gefunden wurden.

a) *Abhängigkeit der Molarprozente der Silikat- und Hydroxylionen in Aluminium- und Eisen-Verbindungen des Bodens von den Silikat- und Hydroxylionenkonzentrationen in der Lösung*

Wie Correns [10 11] zeigte, werden bei der Verwitterung die Ionen der primären Mineralien zunächst echt (ionogen) gelöst und anschließend aus der Lösung zu sekundären Mineralien ausgefällt. So entsteht bei der Verwitterung von Feldspat, Adular und Tremolit um die Kristalle eine aluminium- und silikatreiche Schicht, deren SiO_2-Gehalt mit steigendem pH-Wert abnimmt. Hieraus geht die Abhängigkeit der Molarprozente der austauschbaren Hydroxyl- und Silikationen von der Hydroxylionenkonzentration hervor.

Mattson [27 28] hat Fällungen von positiv geladenen kolloidalen Aluminium- und Eisen-Hydroxyden und negativ geladenem Siliciumdioxyd-Gel hergestellt und behauptet, daß diese Fällungen isoelektrisch sein sollen („isoelektrische Verwitterungstheorie"). Für die Richtigkeit dieser Theorie ist es wesentlich, daß der isoelektrische Punkt der Aluminium- und Eisen-Hydroxyde zwischen pH = 7,0 bis 8,5 liegt, damit diese Hydroxyde bei der meist saureren Reaktion des Bodens positiv geladen sind (durch Abdissoziation von mehr OH-Ionen als H-Ionen). Van Schuylenborg und

Arens [34] konnten jedoch zeigen, daß zwar der IEP von Hydroxyden, die durch schnelle Ausfällung aus konzentrierten Lösungen hergestellt worden waren, bei schwach alkalischer Reaktion liegt, aber der IEP von langsam und aus verdünnten Lösungen ausgefällten Hydroxyden bei saurer Reaktion liegt. Diese Erscheinung beruht darauf, daß schnell und aus konzentrierten gefällte Hydroxyde Unregelmäßigkeiten im Kristallgitter aufweisen, und daher viele Hydroxylionen schon bei höheren pH-Werten abdissoziieren, während die langsam und aus verdünnten Lösungen gefällten Hydroxyde ein derartig gut ausgebildetes Kristallgitter besitzen, daß die Hydroxylionen sehr fest gehalten werden, und daher ihr IEP ebenso wie der von den entsprechenden Mineralien bei saurer Reaktion liegt. Da bei der Verwitterung nur eine langsame Fällung aus stark verdünnten Lösungen erfolgt, können im Boden ausschließlich Hydroxyde entstehen, deren IEP bei saurer Reaktion liegt, die also bei der alkalischeren Reaktion des Bodens negativ geladen sind. Daher ist, wie van Schuylenborg und Arens folgerten, im Boden eine gegenseitige Fällung dieser negativ geladenen Hydroxyde mit negativ geladener kolloidaler Kieselsäure allein auf Grund der Ladung nicht möglich.

Daß trotzdem beim Vermischen von kolloidalem Aluminium- und Eisen-Hydroxyd mit kolloidaler Kieselsäure Fällungen entstehen, dürfte daher auf der Bildung der Austauschersubstanz Aluminium- und Eisen-Hydroxyd-Silikat beruhen. Diese Annahme wird durch den Befund von Mattson selbst gestützt, daß Aluminium- und Eisen-Hydroxyde um so mehr Kieselsäure zu binden vermögen, je höher die Wasserstoffionenkonzentration ist (Abhängigkeit der Molarprozente der Silikat- und Hydroxylionen in den Festkörpern von der Hydroxylionenkonzentration der Lösung).

b) *Abhängigkeit der Molarprozente der Phosphat- und Hydroxylionen in Aluminium- und Eisen-Verbindungen des Bodens von den Phosphat- und Hydroxylionenkonzentrationen in der Lösung*

Diese Abhängigkeit dürfte den bisher ungeklärten [21] Befund klären, daß die Löslichkeitsgleichgewichte der reinen Aluminium- und Eisenphosphate durch Umsetzung mit Goethit und Kaolinit oder mit Böden vermindert werden. Durch diese Berührung mit Substanzen, die Aluminium- und Eisenionen enthalten, werden nämlich die Molarprozente der Phosphationen verkleinert, und somit auch nach Gl. (2) die Phosphatkonzentrationen in der Lösung vermindert. *In vitro* wurde diese Erscheinung in früheren Gleichgewichtsbestimmungen [31] an gemeinsamen Fällungen von Aluminium- bezw. Eisen- sowie Hydroxyl- und Phosphationen aufgezeigt. Auf diese Abhängigkeit weist auch der Befund hin, daß die von

Aluminium- und Eisenhydroxyd adsorbierten Mengen Phosphat nach der Freundlichschen [24 26] und der Langmuirschen Adsorptionsisotherme [14] mit steigender Phosphatkonzentration zunehmen, und daß in Vegetationsversuchen die relative Lösungsgeschwindigkeit von ausgefällten Aluminium- und Eisenhydroxyden mit verschiedenem Phosphatgehalt mit dem Verhältnis P_2O_5 Al_2O_3 bezw. P_2O_5 Fe_2O_3 ansteigt [12 37 39]. Auch die Beobachtungen, daß ausgefälltes Aluminium- und Eisenhydroxyd mit verschiedenem Phosphatgehalt bei saurer Reaktion ein kleineres Löslichkeitsgleichgewicht [31] oder eine kleinere relative Lösungsgeschwindigkeit [12 29 37] in bezug auf Phosphat besitzt als bei alkalischerer Reaktion, deuten auf diese Abhängigkeit hin. Auf das Vorkommen der Austauschersubstanz im Boden weisen weiterhin die Verfahren [3 29] hin, aus der Menge zitronensäurelöslichem Aluminium und Eisen in einem Boden auf das Festlegungsvermögen für Phosphorsäure zu schließen, ebenso wie die Möglichkeit, durch nesterweise Verteilung von Phosphorsäuredüngemitteln [32] oder durch ihr Ausbringen neben die Saatfurche die Versorgung der Pflanzen mit Phosphorsäure zu verbessern. Schließlich stimmt der Hinweis (Ref. [25], S. 70), daß bei wiederholter Extraktion von Böden eine allmähliche und keine stufenweise Verminderung der gelösten Phosphorsäure erfolgt, und somit keine definierten Phosphate im Boden vorhanden sind, gut mit der Annahme des Vorkommens der Austauschersubstanzen überein.

Wie mehrfach beschrieben wurde [2 5 19 20], sind die stöchiometrisch definierten Verbindungen $AlPO_4.2H_2O$ und $FePO_4.2{,}5H_2O$ nur bei so hohen Phosphat- und Wasserstoffionenkonzentrationen existenzfähig, wie sie im Boden keinesfalls vorkommen. Bei Einwirkung dieser hohen Phosphorsäurekonzentrationen auf Aluminium- und Eisenionen enthaltende Substanzen, z.B. Aluminiumhydroxyd und verschiedene Tonmineralien entsteht daher zwar Aluminiumphosphat oder Aluminiumalkaliphosphat-Doppelsalz [26 35 36], wie röntgenographisch und elektronenmikroskopisch nachgewiesen wurde („Phosphatolyse" der Tonminerale [26]) *. Es dürfte jedoch nicht statthaft sein, zu folgern, daß diese Bildung von stöchiometrisch definiertem Alumi-

* Chang und Jackson [6] haben das Löslichkeitsprodukt von Strengit bestimmt: pK = 33–35. Hemwall [18] brachte Kaolinit mit saurer (pH = 4) Natriumacetat—Essigsäure-Pufferlösung mit Phosphatzusatz ($1{,}15 \cdot 10^{-4}$ *M*) in Berührung und fand, daß nach 3 Wochen Aluminiumkonzentrationen von 0,1 bis $6{,}2 \cdot 10^{-5}$ *M* entstanden waren, und die Phosphatkonzentrationen sich invers dazu (9,35 bis $0{,}58 \cdot 10^{-5}$ *M*) eingestellt hatten, ein Befund, der auf die Bildung von Variscit unter diesen Bedingungen hinweist.

niumphosphat durch doppelte Umsetzung im Boden vor sich geht, und auf dieser Folgerung eine „einheitliche Theorie der Phosphatfestlegung" [22] aufzustellen. Da nämlich in der Bodenlösung bedeutend geringere Phosphat- und Wasserstoffionenkonzentrationen als im Existenzbereich der reinen Aluminium- und Eisenphosphate vorhanden sind, dürften nur die Phosphationen enthaltenden Austauschersubstanzen im Boden beständig sein *.

c) *Abhängigkeit der Molarprozente der Humat- und Hydroxylionen in Aluminium- und Eisenverbindungen des Bodens von den Humat- und Hydroxylionenkonzentrationen in der Lösung*

Flaig und Beutelspacher [13] fanden, daß auch in hochgereinigten Huminsäuren (31maliges Umfällen) unter dem Elektronenmikroskop immer noch anorganische Kolloide vorhanden waren. Diese bestehen, wie Analysen gezeigt haben [1], aus Al_2O_3 und Fe_2O_3 mit verschiedenem Gehalt an SiO_2 und P_2O_5, stellen also die Austauschersubstanz Aluminium- und Eisen-Hydroxyd-Silikat-Phosphat dar **. Wie weitere elektronenmikroskopische Aufnahmen zeigen, wurden bei saurer Reaktion Aggregate mit Huminsäuren gebildet, und bei alkalischer Reaktion, nach Zusatz von *N* Ammoniak wurden die Huminsäureteilchen von den anorganischen Kolloiden abgelöst! Diese Bildung und Auflösung der Aggregate dürfte durch den Austausch von Hydroxyl- gegen Humationen an der Austauschersubstanz Aluminium- und Eisen-Hydroxyd-Silikat-Phosphat-Humat zustande kommen.

Die Bildung dieser Austauschersubstanz wurde ebenfalls von Flaig und Beutelspacher demonstriert: Sie beobachteten unter dem Elektronenmikroskop, daß Schnaittenbacher Kaolin normalerweise keine Huminsäuren adsorbiert. Nachdem aber der Kaolinit mit *N* Ammoniak behandelt worden, und das Ammoniak verdampft war, wurde von Flaig und Beutelspacher besonders an den Kanten und Ecken der Kaolinitkristalle eine Huminsäurenadsorption beobachtet. Dieser Befund könnte vielleicht damit erklärt werden, daß die Kaolinitkristalle bei Einwirkung von *N* Ammoniak oberflächlich sich zu frisch gefälltem, hydratisiertem

* Daß Variscit und Strengit nicht als Mineralien im Boden vorkommen, wird schon aus dem Befund [4] offensichtlich, daß in Vegetationsversuchen reiner Variscit und reiner Strengit etwa 75% der Düngefähigkeit des Superphosphates besaßen.

** Andere Verbindungen, wie z.B. Calciumsalze in einer Korngröße, die elektronenmikroskopisch gerade erkennbar ist, wären nämlich nach 31maligem Umfällen schon gelöst worden.

Aluminium-Hydroxyd-Silikat umwandeln, und hieran die Adsorption von Humationen erfolgt. Möglicherweise könnte dieser Versuch von Flaig und Beutelspacher das Modell für die Entstehung der Tonhumusverbindungen abgeben, weil auch für ihre Bildung im Boden bekanntlich eine neutrale oder alkalische Reaktion notwendig ist zur oberflächlichen Umwandlung der Tonminerale in hydratisiertes Aluminium-Hydroxyd-Silikat-Humat.

d) *Nicht stöchiometrische Mengenverhältnisse der Anionen in den Austauschersubstanzen Aluminium- und Eisen-Hydroxyd-Silikat-Phosphat-Humat als Hinweis für ihr Vorkommen im Boden*

In der Literatur konnten keine Hinweise dafür gefunden werden, ob die bekannte Erhöhung der Löslichkeit der Phosphorsäure durch Hydroxylionen, Kieselsäure oder Humus auf einem Ionenaustausch an Austauschersubstanzen beruht (Abhängigkeit der Molarprozente der Hydroxyl-, Silikat-, Phosphat- und Humationen von den Konzentrationen dieser Ionen in Lösung) oder auf doppelte Umsetzungen zwischen stöchiometrisch definierten Substanzen zurückzuführen ist.

Ein Hinweis, daß die Austauschersubstanzen Aluminium- und Eisen-Hydroxyd-Silikat-Phosphat-Humat Minerale des Bodens darstellen, ist die bekannte Tatsache, daß in allen Aluminium- und Eisenverbindungen des Bodens stets gemeinsam Hydroxyl-, Silikat-, Phosphat- und auch oft Humat-Ionen in *nicht stöchiometrischen* Mengenverhältnissen enthalten sind. Selbst reinste Tonmineralien enthalten immer Hydroxyl- und Phosphationen, ebenso wie die Aluminium- und Eisenhydroxyde aus Böden immer silikat- und phosphathaltig sind, und oft auch Humat enthalten.

Der Austausch der Hydroxyl-, Silikat-, Phosphat- und Humat-Ionen an diesen Austauschersubstanzen im Boden dürfte bedeutend schneller vor sich gehen, als es durch doppelte Umsetzungen an kristallisierten, stöchiometrisch definierten Verbindungen von der Oberfläche her möglich wäre. Infolgedessen dürften diese Austauschersubstanzen für die Pflanzenernährung wichtige Bodenminerale sein. Der Anionenaustausch im Boden verläuft daher ebenso wie der Kationenaustausch z.T. an Austauschersubstanzen. Während die Kationenaustauschersubstanzen (Tonminerale) durch röntgenographische Untersuchungen in den 30er Jahren entdeckt wurden, konnten die (röntgenamorphen) Anionenaustauschersubstanzen erst

durch die Erkenntnisse der physikalischen Chemie aufgefunden werden, die einleitend kurz dargestellt wurden.

ZUSAMMENFASSUNG

In wäßriger Lösung wurden Aluminium- oder Eisen(3+)-Ionen bei Siedetemperatur mit Hydroxyl- und Silikat- oder Phosphat- oder Humat-Ionen unter ständiger Aufrechterhaltung bestimmter Mengenverhältnisse umgesetzt. In den entstandenen Niederschlägen wurden die Molarprozente an Hydroxyl-, Silikat-, Phosphat- und Humat-Ionen in weitem Bereich abhängig von den Konzentrationen dieser Ionen im Gleichgewicht gefunden. Daher sind diese Niederschläge als Anionenaustauscher anzusehen. Es wurde die Vermutung ausgesprochen, daß die Aluminium- und Eisen-Verbindungen des Bodens die gleichen Austauschersubstanzen darstellen, und versucht, diese Vermutung durch Besprechung einiger bodenkundlicher Befunde zu stützen. Es zeigte sich, daß der für die Pflanzenernährung wichtige, schnelle Anionenaustausch an diesen röntgenamorphen Austauschersubstanzen erfolgt, ebenso wie der Kationenaustausch über die in den 30er Jahren entdeckten, kristallinen Tonminerale verläuft.

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LETTER TO THE EDITORS

Kennzeichnung der Aluminium- und Eisen(3)-hydroxydphosphate als Austauschersubstanzen durch Einstellung sehr kleiner Gleichgewichtskonzentrationen

Früher [1] wurde gezeigt, daß die gemeinsamen Fällungen von Aluminium- oder Eisen(3)ionen mit Hydroxyl- und Phosphationen das Kennzeichen der Austauschersubstanzen besitzen, in *weitem* Bereich eine Abhängigkeit der Molarprozente an Hydroxyl- und Phosphationen in den Festkörpern von den Hydroxyl- und Phosphationenkonzentrationen in der Lösung im Gleichgewicht aufzuweisen. Diese Abhängigkeit müßte auch im Bereich sehr kleiner Gleichgewichtskonzentrationen bestehen, wie sie z.B. an trägerfreiem, radioaktivem Phosphat mit Hilfe von Zählrohren gemessen werden können. Eine experimentelle Untersuchung dieser Abhängigkeit auch im Bereich dieser sehr kleinen Phosphatkonzentrationen würde zur Kennzeichnung der Aluminium- und Eisen(3)hydroxydphosphate als Austauschersubstanzen weiterhin beitragen.

Versuche

Zu 2 l destilliertem Wasser wurde so viel trägerfreies, radioaktives Phosphat zugesetzt, daß 14 ccm dieser Lösung 1770 Impulse je 180 Minuten in einem Veallschen Flüssigkeitszählrohr bewirkten, dessen Nachweiswahrscheinlichkeit für trägerfreies P^{32} 10% betrug. Daher finden in 14 ccm Lösung 98 Zerfälle je Minute = 1,64 Zerfälle je Sekunde statt. Da ein Nanocurie (= 10^{-9} Curie) diejenige Menge einer radioaktiven Substanz ist, in der 37 Zerfälle je Sekunde auftreten, und ein Nanocurie $P^{32} = 3{,}6 \cdot 10^{-15}$ g ist, sind in 14 ccm Lösung 0,044 nC = $1{,}6 \cdot 10^{-16}$ g = $5 \cdot 10^{-18}$ Mol P^{32} enthalten. In einem Liter sind daher $1{,}14 \cdot 10^{-14}$ g = $3{,}6 \cdot 10^{-16}$ Mol P^{32} vorhanden.

In mehreren Ansätzen wurden je 100 ccm dieser Lösung unter Ersatz des verdampfenden Wassers zum Sieden erhitzt, mit Bromthymolblau versetzt, und in diese siedende Lösung aus je einer Bürette tropfenweise 10 ccm 0,02 *M* angesäuerte Aluminium- oder Eisen(3)salzlösung und gleichzeitig so viel Natronlauge zugegeben, daß die Reaktion ständig neutral gehalten wurde. Anschließend wurde noch heiß filtriert, und im Filtrat nach dem Abkühlen die Radioaktivität im gleichen Flüssigkeitszählrohr bestimmt. Sie wurde in allen Fällen mit etwa 3100 Impulsen in 180 Minuten nur wenig über dem Nullwert liegend gefunden: 50 Impulse in 180 Minuten je 14 ccm entspricht der Konzentration: $3{,}2 \cdot 10^{-16}$ g = $1 \cdot 10^{-17}$ Mol P^{32} je Liter.

Diskussion

Zu einer Menge von $3{,}6 \cdot 10^{-17}$ Mol radioaktivem Phosphat je 100 ccm wurde also eine Menge von $2 \cdot 10^{-4}$ Mol Aluminium- oder Eisen(3)salz zugesetzt. Da nahezu alles Phosphat ausgefällt worden war, besaßen die Niederschläge das molekulare Verhältnis Al : P oder Fe : P (= Al_2O_3 : P_2O_5 oder Fe_2O_3 : P_2O_5) $= \frac{2 \cdot 10^{-4}}{3{,}6 \cdot 10^{-17}} = 5{,}7 \cdot 10^{12}$. Diesem sehr großen Wert entspricht ein sehr kleiner Molarprozentsatz an Phosphationen in den Niederschlägen, die im Gleichgewicht mit den sehr geringen Phosphatkonzentrationen stehen, die nach der Ausfällung noch in der Lösung vorhanden waren. Daher besteht die einleitend erwähnte Abhängigkeit, die ein Kennzeichen für Austauschersubstanzen ist, auch im Bereich der sehr kleinen Molarprozente und Konzentrationen.

Da es kein stöchiometrisch definiertes Phosphat gibt, in deren Löslichkeitsgleichgewicht derartig geringe Konzentrationen (10^{-17} Mol Phosphat/l) vorhanden sind, ist das Versuchsergebnis als ein weiteres Kennzeichen dafür anzusehen, daß die gemeinsamen Fällungen von Aluminium- oder Eisen(3)- mit Hydroxyl- und Phosphationen Austauschersubstanzen darstellen.

Mit diesem Versuch wird auch gezeigt, daß das bekannte Verfahren der analytischen Chemie, Phosphationen aus einer Lösung durch Zusatz von Eisen(3)salz und Natriumacetat und anschließendes Aufkochen zu entfernen, diese Entfernung der Phosphationen bei genügend großem Eisensalzüberschuß sehr weitgehend bewirken kann.

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